ORIGIN OF THE PRECAMBRIAN PHOSPHORITE DEPOSITS OF PANCHMAHALS DISTRICT, GUJARAT

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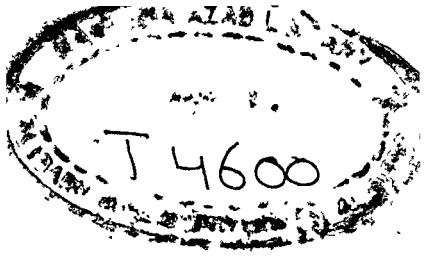

ORIGIN OF THE PRECAMBRIAN PHOSPHORITE DEPOSITS OF PANCHMAHALS DISTRICT, GUJARAT

Syed Rehan Ali

ABSTRACT

The four neighbouring areas for the present investigation have been selected around Chalvad, Gandhra, Ambapani and Ranjitpura areas of Panchmahals district, Gujarat, where phosphorite deposits of low to medium grade are reported to occur within the thick succession of the Precambrian rocks belonging to the Champaner Group of the Aravalli Super Group. An attempt has been made to study the geology, structure, grade of metamorphism, mode of occurrence, stromatolitic assemblages, petromineralogy, geochemistry of the deposits and present a model for their origin.

The phosphatic horizon is confined to Khandia Formation of the Champaner Group. The rock units encountered in the areas include metaconglomerate, quartzite, phyllites, dolomitic limestone, phosphorite, metagraywacke and granitoids occupying the entire southern and western part of the area and are the product of low grade regional metamorphism and comparable with the low grade greenschist facies to chlorite schist facies. The general strike trend of the rocks is NW-SE direction. They have dominantly southernly dips at moderate angles. The rocks around Gandhra form a major anticlinal fold with axial plane trending WNW-ESE to nearly E-W

The following five varieties of phosphorites are recognised :

1. Columnar algal stromatolitic phosphorite
2. Laminated algal stromatolitic phosphorite
3. Pelletal phosphorite
4 Nodular phosphorite
5. Bedded phosphorite

The phosphatic horizon is traceable over a strike length of about 0.4 Km in Chalvad block, 0.7 Km in Gandhra block, 0.4 Km in Ambapani block and 1.2 Km in Ranjitpura block with their horizontal width of 10 to 30 metres. The richest deposits are confined to the Ranjitpura block.

The stromatolitic form species namely *Collenia columnaris, Collenia baicalica, Conophyton, Colonnella and Kusseilla kusiensis* are identified and described.

Petromineralogical studies of these phosphorites indicate collophane and dahllite are the dominant phosphate minerals. Calcite and dolomite are the chief gangue constituents of these phosphorites. Other minerals identified include quartz, feldspar, muscovite, sericite, tremolite, carbonaceous matter and opaques of iron oxides. The scanning electron microscopic study indicate the growth of apatite grains in the calcite showing the replacement of calcite by apatite. Infra-red spectral studies reveal the presence of structural CO_3 and OH ions in these phosphorites. The discrete carbonate has also been detected in these phosphorites.

The bulk chemical analyses of selected samples indicate wide variation in distribution of various chemical constituents. Most common type of phosphorite in the area are characterised by low to moderate concentration of P_2O_5, SiO_2, Fe_2O_3 and FeO, low concentration of MnO, Na_2O, K_2O, Al_2O_3, TiO_2, H_2O^+ and F high concentration of CaO, MgO and CO_2. The sympathetic relationship between CaO and P_2O_5 indicates the formation of stable calcium carbonate. The negative relationship of MgO with CaO and P_2O_5 suggests the replacement of magnesium calcite by calcium phosphate. The higher CaO/P_2O_5, CO_2/P_2O_5 ratios indicate the presence of carbonate apatite and the formation of phosphorite by replacement process of the constituents. Sympathetic relationship of F with P_2O_5 and F/P_2O_5 and F/H_2O ratios approach very near to carbonate hydroxyl fluorapatite. Fe_2O_3/ FeO ratios suggest slightly reducing to fairly oxidizing environment of deposition.

The fixation of trace elements like Cu, Ni, Co, Cr, Pb and Zn seems to the geochemically controlled by the biogenic activity at shallow marine environmental condition. Sr and Pb seems to be structurally combined in apatite lattice, whereas Li and Rb are mainly associated with the lattice of clay minerals.

The ingredients of phosphates are probably derived from the pre-existing Banded Gneissic Complex as a result of their chemical decay followed by the release of phosphorus to the shallow marine water and sediments. The micro-organisms also contributed some phosphorus and help in concentrating the phosphorus at the site of deposition.

The accummulation and deposition of phosphorite in the basin have largely been guided by geologic, biogenic and chemical controls. The proposed model of origin of the phosphorites of Panchmahals is based on the various observations made and their structure, stratigraphy, petromineralogy, stromatoiites and geochemistry of major and trace elements.

The model envisages deposition of these phosphorites in shallow intertidal to shallow subtidal marine environment where the growth of algal stromatolites initiated their accummulation in addition to varying precipitation by almost contemporaneous and progressive replacement of early formed carbonates by calcium phosphate. The occurrence of the variety of phosphorites in the deposits appears to be related to some environmental change in the sites of deposition followed by structural disturbances.

Dedicated to my mother

"Mrs. Qaiser Rizwan"

motivating source of light
behind whatever little success
I have achieved

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CERTIFICATE

This is to certify that **Mr. Syed Rehan Ali** has completed his research under my supervision for the degree of **Doctor of Philosophy** of the **Aligarh Muslim University, Aligarh.** This work is an original contribution to our knowledge of the phosphorite deposits of Panchmahals district, Gujarat and has not been published anywhere.

Mr. S.R. Ali is allowed to submit the work for the Ph.D. degree in Geology of the Aligarh Muslim University, Aligarh.

L.A.K. Rao
Supervisor

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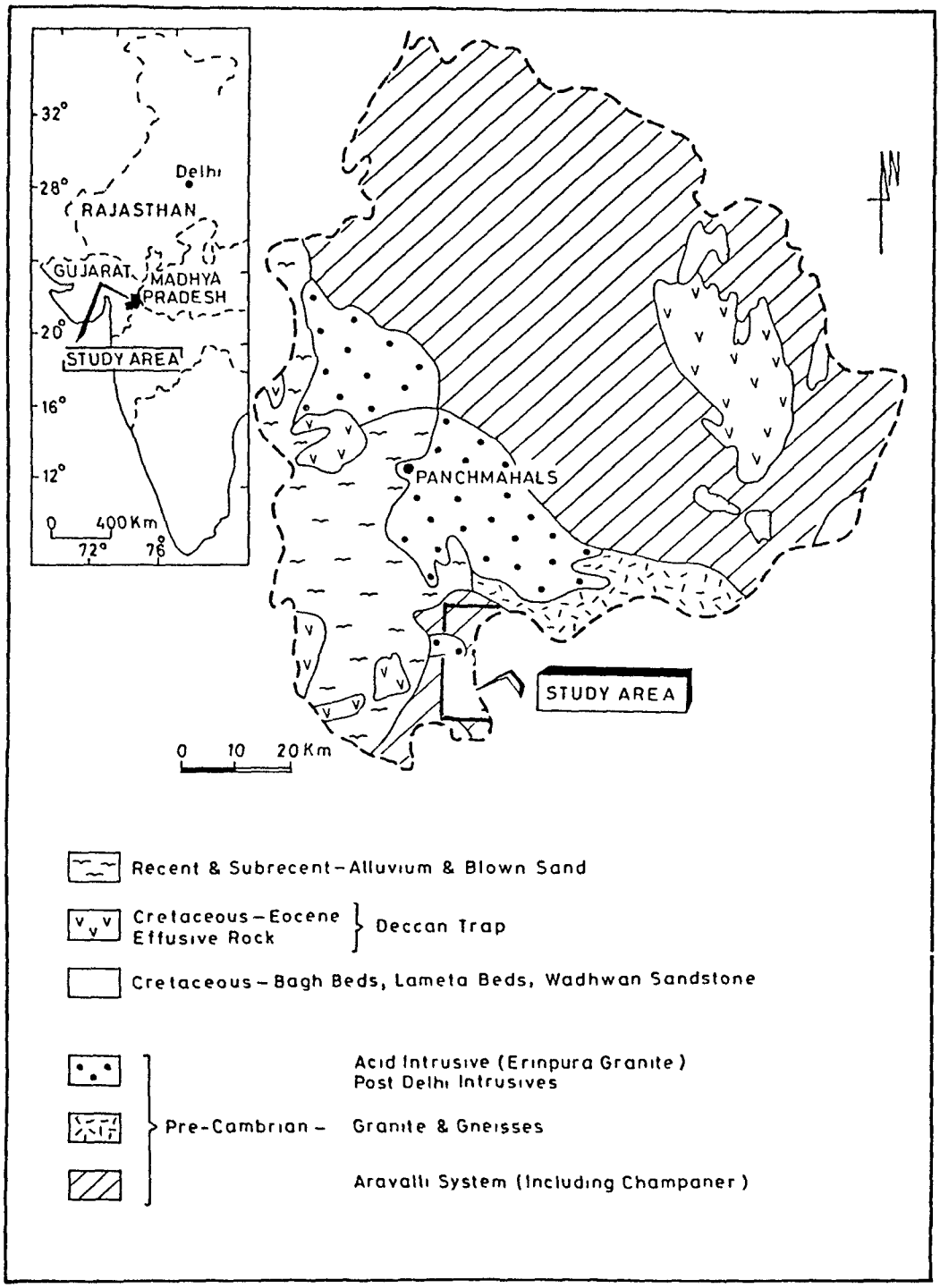

Fig. 1: Location Map of Panchmahals Phosphorite Deposits, Panchmahals District, Gujarat.

CHAPTER-I

INTRODUCTION

GENERAL STATEMENT

The phosphorite occurrences of Panchmahals district, Gujarat were first reported from the Champaner Group belongs to the Precambrian age by the Personnels of Geological Survey of India in the year of 1979-80. These phosphorites on the basis of their litho-association, stromatolitic form species and mineral assemblages etc. are considered to be the extension of the Precambrian Aravalli phosphorites of Udaipur district, Rajasthan. Although the Precambrian phosphorite deposits have been discussed in detail by various workers but a very little attention is drawn for the study of phosphorite deposits of Panchmahals district, in spite of their geological significance. Therefore the present investigation may be considered as the first serious attempt to study the deposits from the view point of their geochemistry, petromineralogy and origin.

LOCATION AND ACCESSIBILITY

The phosphorite deposits of Panchmahals district are located (22°27' : 73°41'30") at a distance of about 103 Km South-west of Panchmahals district, Gujarat. The area is approachable from the Panchmahals town by a metalled and motorable road. The district is connected with all the major cities of the country by rail.

CLIMATE

The climate of the Panchmahals district is semi-arid and the average annual rainfall is ranging from 75 cm to 88 cm since last

five years.

PHYSIOGRAPHY

Physiographically the area can be divided into three main units. viz. (1) undulating hilly area of east- northeast and part of north, (ii) piedmont zone and (iii) western and southern plain. The highest point of the area is Pavagadh in Halol Taluka having the height of 829.36 meters above the mean sea level. The east and the north-east areas are covered with rolling hills having longitudinal steep slopes. The piedmont zone runs all along the periphery of hilly zone. The western plains are flat and are traversed by rivers.

DRAINAGE AND VEGETATION

The main rivers in the region are Mahi, Goma, Kun, Panam and Karad Meshri. Out of which Mahi and Panam are perennial rivers whereas others are emphemeral. Two main dams are constructed for irrigation purpose which are (1) Kadana dam, on river Mahi and (2) Panam dam, on river Panam. The irrigation facilities are very poor and land is not fertile. Only western plains of the area form cultivated land. The main crops of the area are maize and Jawar. The major part of the district is covered by forest having Teak, Eucalyptus, Mahua and other fast growing fuel wood.

STATUS OF PANCHMAHALS PHOSPHORITES

The discovery of the Precambrian Aravalli stromatolitic phosphorite deposits from Chalvad, Gandhra, Ambapani and Ranjitpura villages of Panchmahals district, Gujarat by the personnels of Geological Survey of India, encouraged a widespread exploration for phosphorite in Gujarat. The search for

phosphorite deposits in the region was based mainly on their typical litho-association of dolomitic limestone, stromatolitic structures and tectonic framework, favourable for the deposition of phosphatic material.

The stromatolitic structures and associated phosphorites have been traced so far over a distance of about 3 Km within the crystalline dolomitic limestone bed between Ranjitpura i.e. north of Gandhra and Chalvad villages. The main phosphatic horizon extends for about 1.2 Km in Ranjitpura, about 0.40 Km in Ambapani, 0.70 Km in Gandhra and about 0.40 Km in Chalvad, with their horizontal widths varying from 10 m to 30 m. The phosphatic material is confined mainly to the algal structures and occur associated with dolomitic limestone.

SCOPE AND PURPOSE OF INVESTIGATION

With a view to understand the mechanism and physico-chemical conditions in which the phosphorite deposits of Panchmahals were formed, the present investigation has been taken up. The present work by the author has been directed not only to study the stratigraphy, structure etc. of the area but also to make a detailed investigation of these phosphorites with respect to their geochemistry, petromineralogy, mode of occurrence and origin.

PREVIOUS WORK

Preliminary studies of the Precambrian stromatolitic phosphorites of Ranjitpura,Ambapani, Gandhra and Chalvad villages of the Panchmahals district have been carried out for the first

time by Dwivedi, G.N. (1981). Systematic geological mapping around Panchmahals was carried out by Yellur, D.D. et al., (1966), Rao, A.D. and Prasad (1966), and Gopinath, K. (1971). The stratigraphy and structure of the Precambrians around Baroda and Panchmahals districts, Gujarat have been discussed by Gopinath et al., (1973). Search for basemetals and phosphorite deposits in parts of Baroda and Panchmahals district were carried out by Gopinath and Krishnamurti, K. (1968). Sequence and nomenclature of the Aravallis (*Champaner series*) around Shivrajpur, Panchmahals district was carried out and discussed by Rasul, S. H. (1964).

METHODS AND PRESENTATION OF WORK

The present work on the phosphorite deposits of Panchmahals involves a detailed study of various aspects related to geological setting, geochemistry, petromineralogy and origin of the phosphorite deposits. The present investigation includes the followings:

1) **FIELD INVESTIGATION**

The total duration of field work in the study area was for more than six months. Representative phosphorite and other associated rock samples were collected carefully for the petrographic, mineralogic and chemical analyses.

2) **LABORATORY INVESTIGATION**

i) **Petrographic and mineralographic studies**

Petrographic and mineralographic studies of 150 thin sections of the phosphorites and other associated rocks were

carried out under transmitted light.

INFRA-RED ABSORPTION SPECTRAL STUDY

Infra red spectral analysis of samples were carried out between 2.5 μ and 15 μ wave length region, using Perkin Elmer Model 137 Infra red spectrophotometer to get the information about the compositional characteristics of the apatite group of minerals. KBr pellets were used for IR spectra.

SCANNING ELECTRON MICROSCOPIC STUDY

The scanning electron microscopic study of representative samples of phosphorites of the Precambrian stromatolitic phosphorite of Panchmahals district was made, using the Hitachi S-2300 scanning electron microscope at various magnifications to see the shape, size and nature of the grains of phosphate minerals.

ii) **Chemical Analyses of Rock Samples**

Systematic chemical analyses of the phosphate rock for the quantitative determination of major, minor and trace elements were carried out by using Atomic Absorption Spectrophotometer, Flame photometer, Spectrophotometer and volumetrically.

ANALYTICAL PROCEDURE

On the basis of thin section study, a total number of fifty

eight samples of phosphorites and associated rocks were finally selected for the chemical analyses. The selected samples have been crushed and grinded in an automatic grinder to -200 mesh size and a small quantity of each sample was taken after coning and quartering for chemical analyses following the procedure given by Shapiro, L. and Brannock, W.W. (1962). The procedure followed is described briefly as follows:

Most of the rock constituents are determined with the help of the two solutions conventionally called SOLUTION-A and SOLUTION-B. The former one is used for the determination of SiO_2 and Al_2O_3 while the later one is used for the determination of TiO_2, Fe_2O_3, MgO, CaO, Na_2O, K_2O and P_2O_5.

SiO_2 : Determined by molybdenum blue method.

Al_2O_3 : Determined by calcium aluminium alizarin red-S complex method.

Fe_2O_3 : Determined by developing orange colour with Orthophenanthroline.

TiO_2 : Determined on a yellow colour produced with iron.

MnO : Determined on the pink colour of permanganate complex developed by oxidation with potassium periodate.

P_2O_5 : Determined by yellow molybdovanado phosphoric acid complex.

All the above mentioned oxides were determined at different wavelengths on Ultra Violet Spectrophotometer (Model Beckman D_2) in the chemistry department of A.M.U. Aligarh.

Cao and Mgo : Determined volumetrically using disodium methylene

diamine tetra acetate (EDTA).

Feo	:	Determined volumetrically with a standard dichromate solution using diphenylamine sulfuric acid as the indicator.
P_2O_5	:	Also determined volumetrically which shows almost the same results as obtained calorimetrically with the exception recorded in a few samples having variation of ± 0.25 percent P_2O_5.
CO_2	:	Determined volumetrically.
F	:	Determined by titrating against $KMnO_4$(N/10).
Na_2O & K_2O	:	Determined by using flame photometer and Atomic Absorption Spectrophotometer.
Loss on Ignition (LOI)	:	Determined by heating of the sample powder in a glass tube at about 800°C.

TRACE ELEMENT ANALYSES

The solutions for the quantitative determination of Cu, Ni, Co, Rb, Li, Cd, Pb and Zn were prepared by dissolving one gm of rock sample powder in 20 ml of 1:1 HNO_3 and diluted to 100 ml with distilled water. The trace element concentrations were determined using Atomic Absorption Spectrophotometer (G.B.C. model No. 902) by using the procedure outlined by Ward, F.N. et al., (1969) and Angino, E.E. and Billings, G.K. (1967). The wavelength used for the individual elements is given below.

Wavelengths used in Atomic Absorption Spectrophotometer.

Elements (in ppm)		Wave length (in nm)
Cu	-	324.7
Ni	-	241.5
Co	-	240.7
Pb	-	283.3
Zn	-	213.9
Cr	-	357.9
Sr	-	460.7
Rb	-	780.8
Li	-	670.8
Cd	-	228.8

All the data were standardized against U.S.G.S. standards BCR-I, BCR-32, W-1, Sy-1 and SRM-120C. To avoid any error in the determination, double and triple runs were made by taking different samples from the same specimen powders. After the chemical analysis, the data were fed to VAX 11/780 computer for calculation and correlation of the element ratios of petrogenetic significance and correlation coefficient between major and minor oxides as well as trace elements. The mean and standard deviation values of various oxides and trace elements were also noted.

A C K N O W L E D G E M E N T S

Firstly, let the author thank to Allah, the Almighty for it is due to Him only, this work has been completed amidt a number of hurdles and obstructions.

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CHAPTER-II

STRATIGRAPHY AND GEOLOGICAL SET-UP

The phosphorite occurrences associated with the stromatolitic structures were recorded within the dolomitic limestones, belonging to the Champaner Group of the Aravalli Supergroup of the precambrian rocks of Panchmahals district, Gujarat.

The Champaner series of rocks occur as isolated patches, occupying about 850 sq. Km. area around Baroda and Panchmahals districts. These rocks are enclosed to the south-east and north by intrusive granite and to the north-west by infra-trappeans and deccan traps. Numerous isolated out-crops inlier of various dimensions which are structurally and lithologically similar to the main belt of the Champaners were observed within the granitic terrian almost upto northern boundary of the granites with the Aravalli metasediments (Gopinath, et al., 1973) south of Devgad Baria. The Champaners are classified into lower and upper Champaners separated by a distinct unconformity as given in Table-I (Gopinath 1971).

Table I

	Champaner Belt (sw part of Area)
Upper Champaner	-Phyllites with calcareous intercalations towards bottom. -Quartzite and grits with phyllitic intercalations, Mn-bearing towards top. -Jaban conglomerate.
	----------Unconformity----------
Lower Champaner	-Quartzite with phyllitic intercalations. -Dolomitic limestone (stromatolitic). -Phyllites and mica schist.

	-Quartzite and quartz schist.
	-Bhamaria conglomerate.
----------Unconformity----------	
	-Mica schist.
Pre	-Quartzite and grit.
Champaner	-Mica schist and phyllites.
	-Quartzite and grit.
	-Conglomerate.
----------Unconformity----------	
(?) Lower Aravalli Gneissic Suit	-Quartzite and mica schist with intercalations of grit and conglomerate paragneisses.

The systematic geological mapping around Panchmahals district, Gujarat was carried out by Dwivedi (1981)). The stratigraphic succession around Gandhra, Panchmahals district, as established by Dwivedi, (1981) is given in Table II.

Table II

	Rajgadh Formation	Dolomite Quartzite Metasubgraywacke Phyllites
C		
	Shivrajpur Formation	Calcareous quartzite Manganiferous phyllite
H		Phyllites
	Jaban Formation	Quartzite Metagraywacke
A		Metaconglomerate
	Narukot Formation	Quartz-sericite schist Quartzite
M		Phyllites
		Quartzite
		Metaconglomerate
P		
	Khandia Formation	Quartzite Metagraywacke
A		Quartz-biotite schist
		Quartzite
N		Dolomitic limestones with phosphorite, associated with stromatolite.
E		Metagraywacke
		Phyllites
		Quartzite
R		Metaconglomerate
	Lambhia	Mica schist

Formation	Quartzite Metaconglomerate Migmatite Metagraywacke

The folded metasediments of the Champaner group can be divided into six Formations, viz. Lambhia Formation, Khandia Formation, Narukot Formation, Jaban Formation, Shivrajpur Formation and Rajgadh Formation. The phosphorite bearing horizon confined to the Khandia Formation which is overlain by Lambhia Formation and underlain by Narukot Formation. The rock units encountered in the area of interest belonging to Khandia Formation include metaconglomerate, quartzite, phyllite, metagraywacke and dolomitic limestone with stromatolitic phosphorite. The geological setting and distribution of phosphorite deposits around Gandhra are shown in Fig. 2 and described as follows:

DOLOMITIC LIMESTONE:

The dolomitic limestone containing stromatolitic phosphorite is exposed mainly in the valley areas, south of Sansuva, extending westwards from south of Bhabher to Ranjitpura, then swerving SSW through Gandhra, almost upto Chalvad and again turning south-east up to Vau. The dolomitic limestone is overlain by quartzite and underlain by phyllite. In the study areas the dolomitic limestone is grey to buff in colour and fine to coarse grained, poorly bedded and often containing siliceous or manganiferous and ferruginous material in varying proportions. The general strike trend of this rock unit is NW-SE and dipping

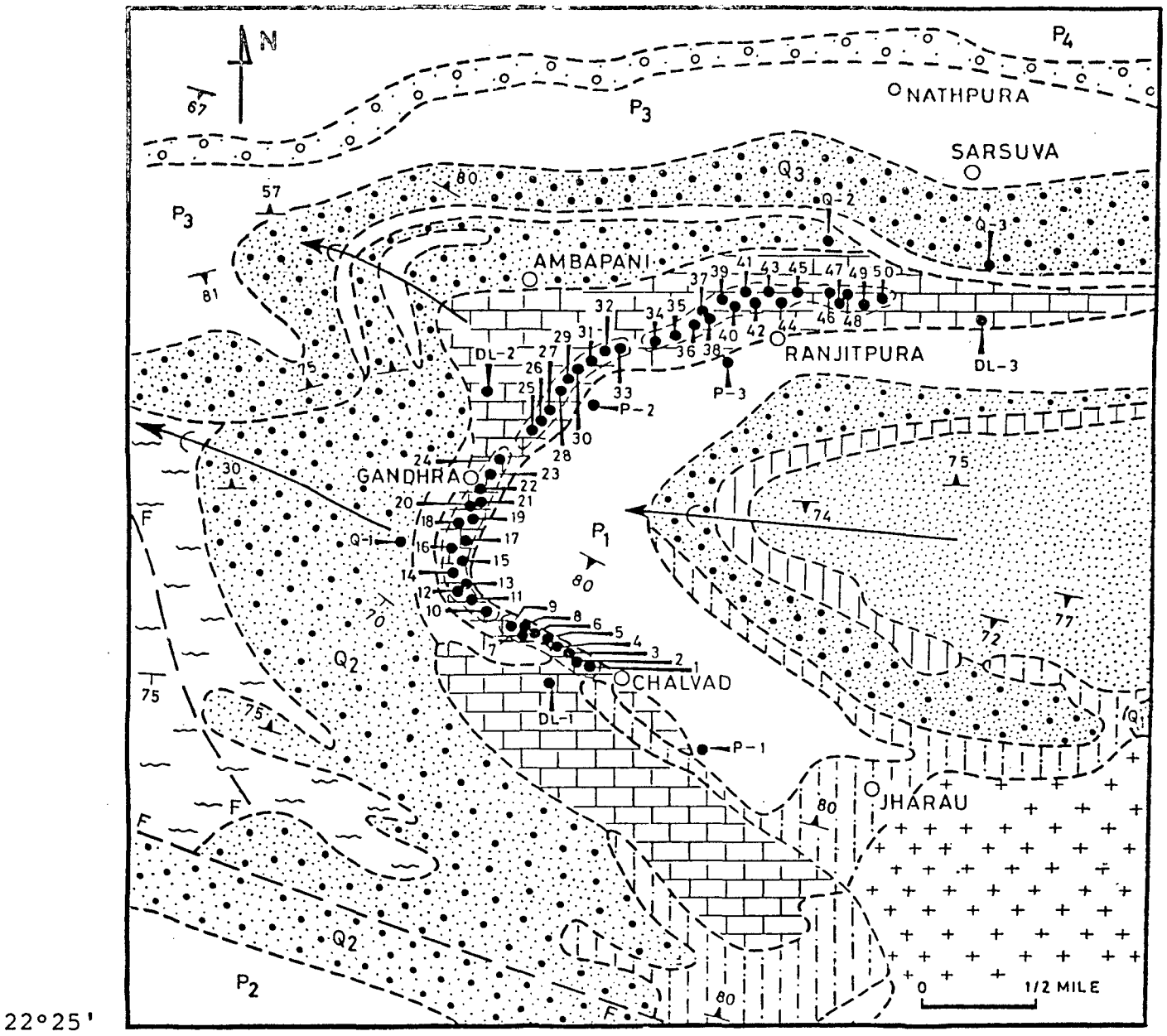


Fig. 2: Geological map showing phosphorite occurances of Panchmahals district, Gujarat.

towards south and SW at an angle of 45° in the southern portion and 16°N in northern portion of the area (Fig. 2).

QUARTZITE

The overlying quartzite is hard, well bedded and at places crystalline in nature. It is dirty white to buff in colour, composed mainly of quartz with minor amount of calcite, dolomite, feldspar and ferruginous matter. The general strike of the quartzite is NNW to SSE in the southern portion and nearly E-W in the northern portion of area. In the southern portion of the area it dips at 60° and 80° towards south and SW whereas in the northern portion it dips 70° and 85° towards north and north-east.

PHYLLITES

The underlying phyllites are grey to light green and ash grey in colour, composed mainly of quartz, feldspar, mica, chlorite and carbonaceous material. The phyllites are fine to medium grained. Cleavages are well developed and at places bedding is defined by compositional colour banding. The general strike trend of the rock is roughly N-W dipping towards west at an angle of 74° in the north-east of Gandhra.

VEIN QUARTZ:

Veins of translucent crystalline quartz occur mostly in the phyllite, quartzite and rarely in dolomitic limestone. These quartz veins vary in thickness from a few cm to two metres and

can be seen mainly along the bedding and foliation planes of the rock. At places these quartz veins show cross cutting relations with the dolomitic limestone (Pl. I, Fig. 1). Occasionally light green tremolite and small crystals of secondary quartz are also found in small cavities within the quartz veins.

STEATITE VEINS:

Thin veins and stringers of low grade steatite are also encountered within the dolomitic limestone. The ferruginous impurities by alteration and leaching have produced thin powdery coating of yellowish or reddish brown limonitic dust.

S T R U C T U R E

The Precambrian rocks of the region show widely varying structural pattern from repeated period of deformation and accompanying emplacement of igneous rocks. The metasediments of the Champaner belt have been subjected to at least two phases of deformation, finally resulting in the present framework and composed of a rather broad, moderately WNW plunging miniature anticlinorium in the central part with a somewhat similar synclinal structure in the north. In the southern part, profuse faulting presumably as a result of the interaction of two folding phases tend to make the delineation of the structural elements here rather difficult as discussed by Gopinath (1973). The Pre-Champaner (F_1) folding phase has resulted in the development of very tight, overturned and isoclinal folds in the area to the south-west of Jambughoda. The axial trace characterised by ENE-WNW trend with steep southernly dip of axial planes.

The general pattern of the Champaner folding (F_2) is that of a moderately WNW-plunging sigma-shaped miniature anticlinorium exposing the older gneisses and schists in the core, south of Pani mines and west and south-west of Jambughoda. The folds are of more open nature with axial planes trending WNW-ESE to nearly east-west and dipping 70° to near vertical invariably northwards located nearer to the fold axis and kinematically related to their development with a number of longitudinal faults. Transverse faults, cutting across the overall tectonic grain, show two main trends NNW-SSE and NNE-SSW. The existance of third deformational phase is suggested by two small, rather open, north plunging synclinal structure in the northern part of the Champaner belt (Gopinath, et al., 1973).

STRUCTURAL ELEMENTS

The structural elements around Gandhra, Panchmahals have been identified and described as follows :

A. NON-TECTONIC STRUCTURE :

1) **BEDDING OR STRATIFICATION PLANE (S_1) :** The bedding planes are represented by colour or compositional banding in the quartzite. The dolomitic limestone is also thickly bedded with some pronounced foliations developed parallel to the bedding plane. The general strike trend of the beds in area is E-W with normal dips of 65° to 80° towards north and north-east (Fig.2) in the northern part. Whereas the trend becomes NW to SE with dips 70° to 80° towards south and

south-west in the southern part. The strike trend continues to be the same in central part but the dips vary between 75° and 80° towards west.

2) **AXIAL PLANE/PLANER STURCTURE AND FRACTURE CLEAVAGE (S_2 & S_3)** The axial plane foliation (S_2) is well developed in the phyllites and quartzites of the area where it is marked by the parallel arrangement of flaky minerals. Bedding (S_1) is obliterated at places by S_2. The axial planes trending WNW-ESE to E-W and dipping about 70° to near vertical towards north. The strike of S_3 varies from N 70° NW to N 85° NW and cleavage plane dips steeply 65° to 85° WNW.

B. TECTONIC STRUCTURES

1) **JOINTS :** Joints are well developed in the dolomitic limestone and quartzite of the area of interest. Three sets of joints viz. strike, dip and oblique joints are developed in dolomitic limestone of the area (Pl. III, Fig. 2). The joints in quartzite are filled up mainly by the manganese and jasper, whereas those in the dolomitic limestone are mainly silicified. The strike joints in the dolomitic limestone change their direction with strike plane as follows :

i) NNE-SSW to NE-SW with 50°-65° dipping north-west.

ii) NNW-SSE with 60°-80° dip in NE direction and

iii) Almost E-W with steep dips on either side.

2) **FOLDS :** The microscopic folds are quite common in the area of interest. The general fold pattern is that of a moderately WNW plunging anticlinorium. The dolomitic

limestone is a part of roughly E-W trending major anticline. At places north-south trending folds have also been noticed.

3) **FAULTS** : Some minor faults which are cutting across the overall tectonic grain trending NNW-SSE and NNE-SSW are noticed in the field. These faults appear to be transverse faults.

M E T A M O R P H I S M

The Champaner group of rocks considered to be a part of the Precambrian region in which directed pressure has been the most important agent of metamorphism. The portion of the Champaner rocks falling within the study area primarily composed of metaconglomerates quartzites, dolomitic limestone, phyllites, metagraywackes and phosphorites. They all show the effect of low grade regional metamorphism. Recrystallisation during regional metamorphism is common in all the rock types. There are also the evidence, to believe that during metamorphism the rocks have undergone some cataclastic effect, particularly in the quartzites, dolomitic limestone and phyllites.

Quartzite, occuring on high ridges, is composed largely of recrystallised quartz with some flakes of muscovite. Quartzite of the studied area is generally impure having mica, chert, feldspar with some iron impurities(Pl.IV,Fig. 2). Abraded overgrowth and reworking of quartz indicates secondary silicification of quartzose material during regional metamorphism.

The dolomitic limestone, occurring east of the quartzite ridge around Gandhra area, is mostly recrystallised. The massive dolomitic limestone is also common in Chalvad block. The dolomitic limestone occurring in the region consists of calcite, dolomite, quartz, apatite, sericite, trimolite, chlorite with variable amount of ferruginous matter. The higher CO_2/H_2O and lower H_2O/CO_2 ratios (Tables XV to XVIII) of these rocks indicate that they were subjected to low grade of regional metamorphism (Agrell, S.O. 1965) in the grade of greenschist facies without significant changes in mineralogic Character of the apatite.

The phyllites, exposed north to north-west and east to south-east of the Gandhra area, are generally foliated. The nature of the phyllites is chloritic in the eastern and maganiferous in the northern part of the study area. The mineral assemblages, viz. quartz, feldspar, rutile, apatite, sericite, chlorite etc. could be seen under microscope. These mineral assemblages reach to chlorite schist facies from low grade greenschist facies.

Chapter-III

NATURE AND MODE OF OCCURRENCE OF PHOSPHORITE

The Precambrian phosphorite deposits of Panchmahals district, Gujarat show a great variation in their mode of occurrences. They occur as discontinuous lenses and bands, found associated with the dolomitic limestone of the area.

On the basis of physico-morphological features, the phosphorite deposits of Panchmahals have been classified into the following varieties :

(1) Columnar stromatolitic phosphorite

(2) Laminated stromatolitic phosphorite

(3) Pelletal phosphorite

(4) Nodular phosphorite

(5) Bedded phosphorite

1) COLUMNAR STROMATOLITIC PHOSPHORITE

The columnar stromatolitic phosphorites are dark grey and greyish to whitish grey in colour and are composed of alternating convex laminae of phosphate and carbonate, enveloped in a sheath of phosphate. This laminated arrangement however is not regularly developed throughout the area. The algal columns dominantly composed of carbonate with thin phosphate laminae. The phosphatic component of the stromatolite is composed mainly of collophone and carbonate (calcite and dolomite). The boundary between collophane and calcite is often gradational suggesting replacement of the latter by the former. The algal stromatolites

stand prominantly on the weathered surface of the dolomitic limestone due to their greater resistance to weathering (Pl.II, Fig. 1 and 2). The columnar stromatolites are most common in the area and mainly confined to the northern and north-western part of Gandhra block (Pl.III, Fig. 1) and northern part of Ranjitpura block.

2) LAMINATED STROMATOLITIC PHOSPHORITE

The laminated stromatolitic phosphorites are recorded only from Gandhra and Ranjitpura deposits. They are composed mainly of laminations of phosphate and carbonate. The thickness of individual lamina varies from one mm to one cm. The laminae of phosphate are parallel to the bedding of the dolomitic limestone. The laminated stromatolitic phosphorite can be seen in north-western part of the Gandhra (Pl.III, Fig. 3) and central part of Ranjitpura. These laminated stromatolitic phosphorite are of limited extend both laterally as well as vertically.

Microscopic study of the laminated phosphorite shows that the phosphate laminae of the stromatolites are composed of collophane, which is dark brown to light greyish brown and crypto-crystalline to micro-crystalline in nature. The carbonate laminae are composed of medium to fine grained calcite and dolomite. A careful examination of the collophane-calcite boundary indicates that the fine collophone grains are interspersed with calcite grains (Pl.VI, Fig. 2) suggesting grain to grain replacement of calcite by collophane. Often the

collophane mass contains cluster of calcite grains which indicate that they are the relicts of carbonate laminae.

3) PELLETAL PHOSPHORITE

The phosphorite pellets are mainly embedded in dolomitic groundmass. The pellets are elongated in shape varying in length from 2 to 60 mm and 1 to 6 mm in breadth in the study area. These pellets are found to occur parallel to the bedding plane of dolomitic limestone. This variety of phosphorite can be seen in the central part of Gandhra and north-eastern part of Ranjitpura.

4) NODULAR PHOSPHORITE

The phosphatic nodules, ellipsoidal in shape are composed mainly of fine grained phosphatic material and embedded in dolomitic limestone. These nodules vary in size from 1 to 3 cm in length and 0.5 to 1 cm in width. The nodular phosphorite is mainly confined to the southern part of Gandhra and in the south-western part of Ranjitpura.

5) BEDDED PHOSPHORITE

Massive bedded phosphorite, in true sense, is hardly seen in any of the phosphorite deposits of the area. However, bedded looking phosphorites are found in parts of the Ranjitpura block whereas in rest of the deposits it is not traceable. The bedded phosphorite occurs parallel to dolomitic limestone. They have their laminae composed of phosphate and carbonate. The thickness of bands vary from 1 cm to 2 cm. This phosphorite variety

has probably been developed due to the intense deformation of columnar stromatolites in the area. It seems possible that the development of such variety is due to the rolling of the columns parallel to the bedding. This might have been caused by gravity tectonics at the time when the phosphate horizon was not fully lithified. Due to this the columnar stromatolites were laid down and got flattened along the bedding plane due to parallel shearing of layers. These bedded phosphorite are very similar to the bedded phosphorite of Udaipur district,Rajasthan (Chauhan, D.S. and Sisodia, M.S. 1981).

MODE OF OCCURRENCE OF PHOSPHORITE DEPOSITS

In order to ascertain the distribution of the phosphorite deposits, the mode of occurrence of these phosphorite deposits has been discussed in detail. Their geological set up, structure and distribution is given in Fig. 2.

The phosphorite occurs as discontinuous band extending for about three kilometers along its strike with a thickness varying from 10 to 30 meters. Thickening and thinning of the phosphorite horizon is common feature all along the phosphate bearing dolomitic limestone unit. There is wide variation of P_2O_5 concentration in various bands and bodies of phosphorite but the richest portion (about 20% P_2O_5) is confined to the Ranjitpura where it is composed of columnar and laminated algal stromatolitic phosphorite. The dark bluish grey microsphorite possibly carbonate apatite occurs as streak, nodules, patches,

laminae within almost phosphate free dolomitic limestone. The phosphatic bodies occur as discontinous lenses and bands within the dolomitic limestone unit at Ranjitpura, Ambapani, Gandhra and Chalvad villages in the form of i) columnar algal stromatolitic phosphorite (Pl.III, Fig. 1) with main concentration in algal column ii) as pellets and interclasts in a non-phosphatic matrix as in central and north-eastern part of Gandhra iii) as laminated and bedded phosphorite, occuring parallel to dolomitic limestone and iv) disseminated and nodular bodies set almost in non-phosphatic dolomitic matrix.

CHAPTER-IV

BIOTA OF STROMATOLITIES

INTRODUCTION

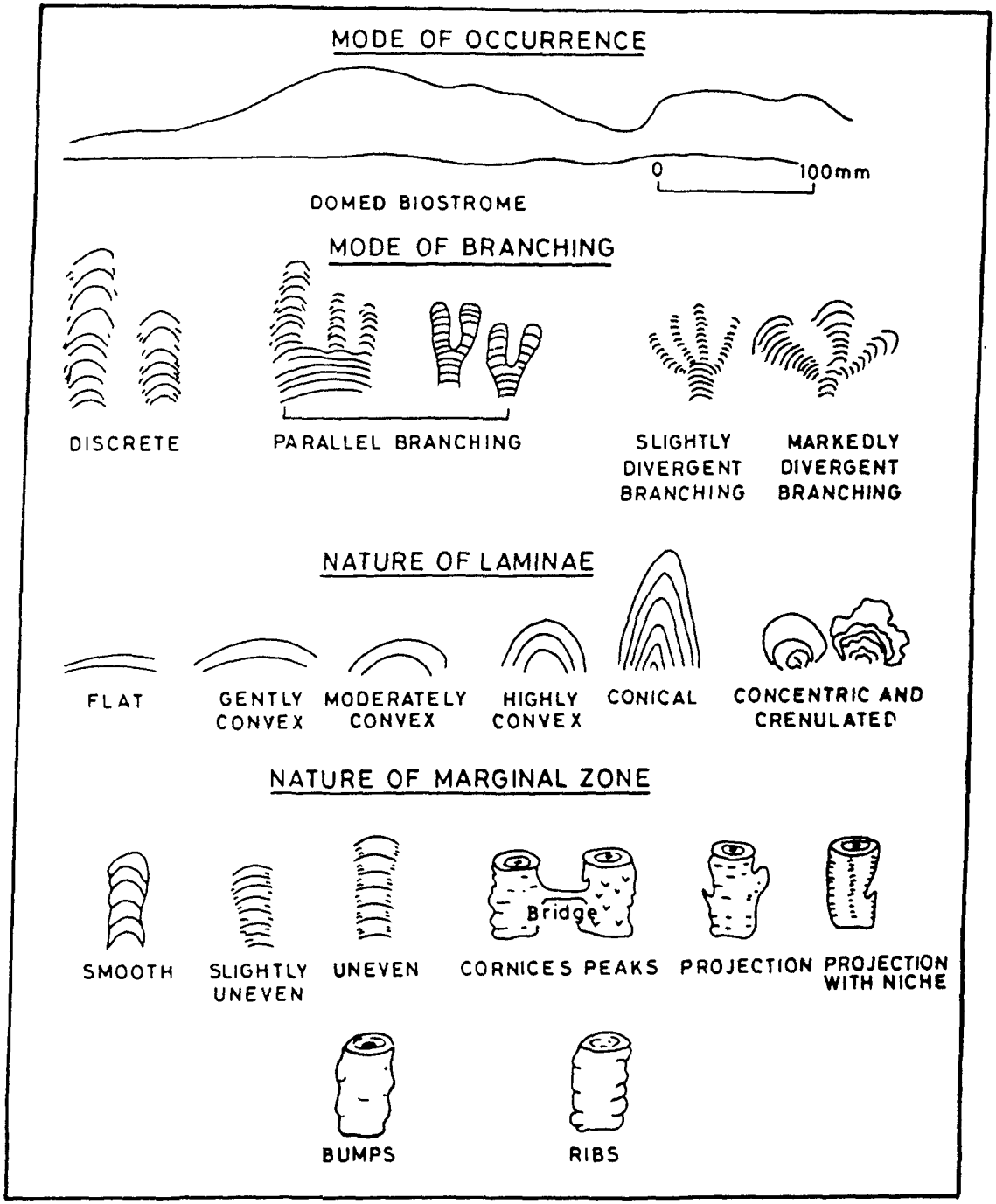
Stromatolites are organosedimentary structures produced by the carbonate precipitations and sediment binding activities of the successive mats of algae, predominantly the blue green algae as defined by Black, M. (1933), Monty, C.L.V. (1967) and Gebelein, C.D. (1969). The term 'Stromatolite' is now used essentially on the genetic connotation of algal stromatolites (Raaben, M.E. 1969; Cloud, P.E. and Semikhatov, M.A. 1969; Walter M.R. 1972).

Studies carried out by Maslov, V.P. (1937), Semikhatov (1962), Komar, V.A. et al., (1965), Raaben (1969) indicate their usefulness in stratigraphic correlation and zonation in ancient sediments especially the late Precambrians. Based on these studies, they established the different assemblage zones of stromatolites and divided the Proterozoic (Upper Precambrian) as:

			(Age in Million Years)
Vendian		....	(570 - 670 m.y.)
	Upper	....	(670 - 950 m.y.)
Riphean	Middle	....	(950 - 1350 m.y.)
	Lower	....	(1350- 2700 m.y.)
Pre Riphean		....	(1650- 2700 m.y.)

Such environmental and ecological significance might help in fixing target areas in search of phosphorites.

The stromatolites from Panchmahals were first reported by



(After Walter, 1976)

Fig. 3: Some important characters of stromatolites.

Dwivedi (1981). This chapter deals mainly with the identification and classification of various stromatolitic form species of the study area and their stratigraphic correlation with other precambrians stromatolites of the world. Palaeo-environmental conditions for the formation of these phosphorites are also discussed.

SALIENT FEATURES :

The following features of the stromatolites were noticed during the course of their study in the feild :

1. The stromatolite have developed laminated and biogenic sedimentary structures, all laminae surface being convex upwards, i.e. the convexity of the laminae is always towards the top side of the bed in which they occur.
2. Laminae, conformable with the bedding of dolomitic limestone and rarely cut across the bedding.
3. The stromatolitic structures are invariably thin and narrow at the base but become thicker and wider towards the top during later stages of their growth.

CLASSIFICATION AND NOMENCLATURE

The term 'stromatolith' was originally used by Kalkowsky, E. (1908) as a purely descriptive term to cover a variety of attached laminated structures in carbonate rocks whether or not of biogenic origin. Pia, J. (1927) used term 'stromatolithi' to inculde all attached columnar forms and the term 'Oncolithi' to include unattached nodular form, both together comprising the family 'sporangiostromata'. *Collenia, Crtyptozoon* and *Weedia* are

classed under the subfamily *'stromatolithi'* whereas *Osagia, Ottonosia* and *Pyenostroma* are placed under the subfamily *'Oncolithi'*. Fenton, C.L. and Fenton, M.A. (1937), Maslov, (1937), Cahen, L.J.A. and Mortelmans, G. (1946), Rezak, R. (1953) and several other used the stromatolites for local stratigraphic correlation.

The stromatolites examined in the area are classified based on their shape, morphological features, organisation of the column, type of branching, space of growth of lamination etc. as suggested by Raaben (1969), Cloud and Semikhatov (1969) and Komar (1966). Following is the general classification given by Raaben (1969).

1. Super Group Conophytonida - (non branching dicrete cylindroidal columns) e.g.*Colonnella, Conophyton*.
2. Super Group Kussiellida - (passively branching cylindrodal columns) e.g. *Kussiella kussiensis*.
3. Super Group Tungussida - (actively branching columns widening upwards, cuplike with divergent axes) e.g. *Baicalla, Tungussida*.
4. Super Group Gymnosolenida - (actively branching paeudocylindroidal columns with axes roughly parallel, and having prominent smooth walls e.g. *Miniasia*.

The non-branching Conophytonida include two groups *Conophyton Maslov* and *Collonella Komar*. The Conophyton is distinguished from the *colonnella* by the presence of a distinct axial zone formed by thickening of microstroma which are of

colonial nature.

The Kussiellida is characterised by subcylindrical columns, frequently elongated and irregular in transverse section. These include *Kussiella kussiensis, Kussiella Krylov* etc.

The Tungussida is charaterised by cup like columns, mostly irregular and rapidly increasing in diameter. These include *Baicalia Krylov, Tungussia Semikhatov* etc.

The Gymnosolenida is characterised by actively branching pseudocylindric columns with a well pronounced cylindrical part.

Later Walter (1972, 76) has suggested a modification in the description of the mode of branching of stromatolites. The parallel branching forms are put under three different categories viz.,

i) α - parallel - (Parallel branching without increase in diameter)

ii) ß - parallel - (Parallel branching in which original column widens gradually before branching)

iii) τ - parallel - (Parallel branching in which the original column widens abruptly before branching)

DESCRIPTION OF STROMATOLITES OF THE STUDY AREA

The various stromatolitic form species identified and recognised from the study area include to those resembles *Conophyton, Colonnella, Kussiella kusiensis, Collenia baicalica* and *Collenia columnaris*.

A concise and systematic description of these stromatolitic form species is given below :

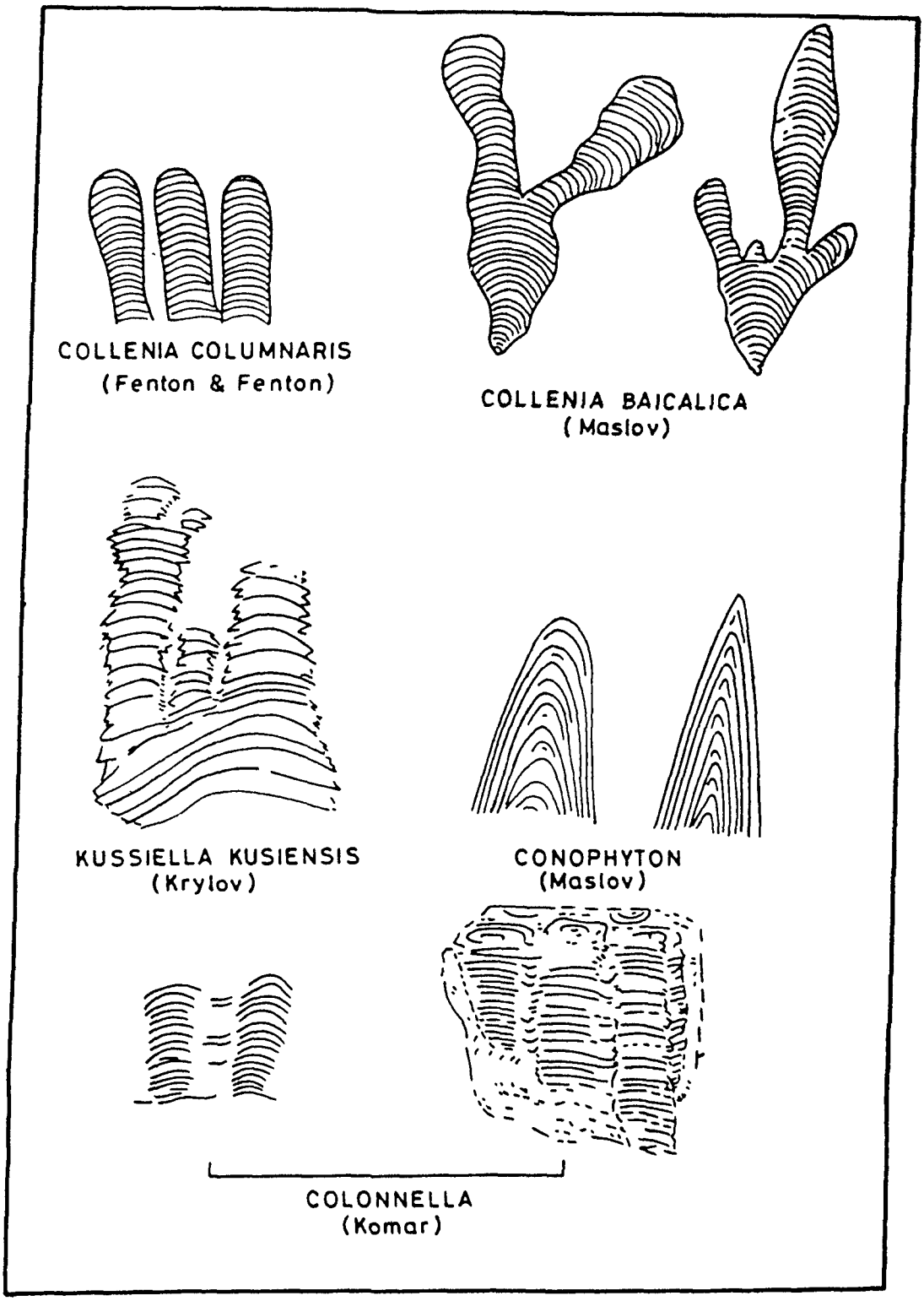


Fig. 4: Different stromatolitic form species found in Panchmahals phosphorites.

Conophyton : (Maslov 1937).

Locality : These stromatolitic form species are identified from Gandhra and Ranjitpura blocks. These form species are characteristic of Lower Proterozoic to Upper Proterozoic (Krylov, I.N.1960; Komar et al., 1965) and serve as index fossils of Precambrian.

Morphology : *Conophyton* is characterised by strikingly conical internal laminae whose apices define as one interrupted by a distinctive axial zone. The subcylindrical column often broad and high but ranging widely in size and display conspicuously and regularly concentric structure in horizontal section (Fig. 4).

Colonnella : (Komar 1966)

Locality : These stromatolitic form species are located in the central part of Ranjitpura and south-eastern part of Gandhra. *Colonnella* is reported from Lower and Middle Riphean. *Colonnella* and *Conophyton* appear to be colsely related with each other.

Morphology : *Collonnela* is characterised by non-branching cylindroidal columns made up of a series of domed microstrata, sometimes slightly thickenning in the central part (Komar 1966). This form can be distinguished from other nonbranching columnar groups like *Conophyton Maslov* by the absence of any prominent axial zone that is the characteristic of *Conophyton* (Fig. 4). The group *Colonnella* includes many species i.e. *Colonnella discreta, Colonnella laminata, Colonnella riasiensis* etc.

Kussiella kusiensis : (Krylov 1963)

Locality : This form species resembles that described by Krylov, (1963) and identified from Ranjitpura and Ambapani. *Kussiella kusiensis* is also a characteristic form of Lower Riphean.

Morphology : *Kussiella kusiensis* is characterised by branching cylindroidal columns in which the original columns break up into two or three branches of smaller diameter. The daughter columns grow vertically upward and are parallel to each other. The laminae are more or less even and of variable thickness that varies from 100-150 microns for the light coloured laminae and 50 to 70μ for dark one.

Collenia baicalica : (Maslov 1937)

Locality : This is the most common form species in the area of interest found in patches forming biohermal phosphorites deposits. This form species of stromatolite is a characteristic form of Lower Riphean.

Morphology : *Collenia baicalica* is mainly characterised by dichotomous, irregularly vertical branching and their broad stem usually break upward into narrow branches as shown in Fig.4.

Collenia Columnaris : (Fenton and Fenton 1937)

Locality : *Collenia columnaris* can be seen in Chalvad and Gandhra villages and is generally non-phosphatic in nature. Often outer rims of the column are coated with phosphatic material and restricted to the dolomitic limestone. *Collenia columnaris* is considered to be characteristic form of the Lower Riphean.

Morphology : This form species resembles to those described by

Fenton and Fenton (1937) and Valdiya, K.S. (1969), occurs as discrete vertical columnar structures which normally grow perpendicular to the bedding. The columns range in height between 2 and 14 cm and the width ranges between 0.75 to 1.5 cm.

ENVIRONMENT AND STRATIGRAPHIC AGE OF PHOSPHATIC STROMATOLITES

Stromatolites are good indicators of environment as has been established on the basis of recent stromatolites (Black, 1933; Logan, B.W. et al., 1964; Gebelein, 1969). These workers believe that stromatolites are found to occur in intertidal to supratidal conditions. The stromatolites form are mainly controlled by environmental factors.

Many earlier workers (Black, 1933; Young, R.B. 1935; Logan 1961; Logan et al., 1964; Monty 1967; Gebelien 1969) have explained that the stromatolites were formed mainly by the trapping and binding activities of detrital carbonaceous sediment to an organic layer of blue green algae. The presence of such algae also influences the stability of the grain size of sediment and surface morphology. The presence of calcite and dolomite in the laminae of stromatolites be attributed to the effect of dumping as well as binding of such grains on to the filaments and unicellular algae, predominantly blue green algae.

Recent studies carried by Achanar, C.W. and Johnson, J.H. (1969), Playford, L. and Cockbain, A.E. (1969), Trompette R. (1969), Awramick, S. M. (1971). Serebryakov, S. N. and Semikhatov (1974) have shown that majority of the world ancient stromatolites are from subtidal setting while only a few have

been reported from intertidal to supratidal environment.

The present study of stromatolites in the study area reveals the presence of *Conophyton, Colonnella, Collenia columnaris, Collenia baicalica* and *Kusiella kusiensis*. These form species of the stromatolites of the area fall in the stratigraphic range of Lower Riphean to Upper Riphean (1650 - 675 m.y.) as described by Dwivedi, (1984). Sarkar, S.N. et al., (1964) assumed a 953 - 1020 m.y. age for the micas in Aravalli Super Group. Except for these controversial age date, no rock has been dated in or around the phosphorite bearing Aravalli metasediments. Consequently Banerjee (1971, 1980) and subsequently Chauhan (1973, 1979) used stromatolite as a tool for biostratigraphic zonation and conclude that the Aravallian phosphorites are Middle to Late Riphean in age on the basis of characteristic stromatolitic form species. Identification of form species *Baicalia* was however questioned by Raaben (1980, 81) described the Aravalli phosphorites an early Proterozoic age. Accodingly on the basis of various stromatolitic form species identified in the area the age of phosphorite of Panchmahals are of an early Proterozoic.

The presence of benthonic algae in the study area clearly indicates a shallow to very shallow depositional environment. It is noticed in the area that phosphatisation is associated with the columnar branching stromatolites whereas the unbranched columns are non-phosphatic or poorly phosphatic, similar to the Udaipur phosphorites. It is logically concluded that the phosphatisation is possibly related to the specific community of

the algae forming stromatolites. As pointed out by Valdiya (1972), the algae must have played a significant role in the localisation of phosphate in dolomite/dolomitic limestone formed in very shallow warm waters of the sea. The columnar structure must have been developed in the intertidal areas as indicated by the inconsistency in the morphology of stromatolites whereas the small isolated laminated algal stromatolitic phosphorite suggest the shallow subtidal environmental conditions.

CHAPTER-V

PETROMINERALOGY

In order to understand the petromineralogical characteristics of the phosphorites and other associated rocks, about 200 representative samples were collected from Panchmahals district, Gujarat. These samples were studied under the petrological microscope and scanning electron microscope. The compositional charateristics of the phosphate minerals were determined by infra red absorption spectroscopy. The minerals identified in these phosphorites and other associated rocks are described as follows :

PHOSPHORITE

It is well known that phosphorite contains more than one apatite like minerals viz., francolite, dahllite, pedolite, gradnolite, wilkeite, ellestadite, staffelite, kurskite, voelckerite, whitelockite etc. Since such wide compositional variation is common, hence it is convenient to use the term collophane as a generic term in phosphorite.

COLLOPHANE

The term collophane has been used extensively in literature to denote very fine micro-crystalline and crypto-crystalline apatite and apatite like minerals found in phosphorites. In general collophane is faintly anisotropic to isotropic and occurs mainly in the form of random subhedral to anhedral grains in the groundmass of calcite and dolomite (Pl VI, Fig. 1). Collophane is

almost exclusively concentrated in the columnar stromatolites. In fact, higher P_2O_5 concentration is observed with higher density of stromatolites, dropping sharply outside this zone. Mineralogically dahllite and francolite are the dominant phosphate minerals. Megascopically, these phosphorites are fine grained, light to dark bluish grey and often brownish in colour. Microscopically these phosphorites are composed of microsphorite which is carbonate apatite, carbonate hydroxyl fluorapatite and carbonate hydroxyl apatite containing calcite, dolomite, quartz and ferruginous matter especially limonite. Under the microscope, the laminated phosphorite shows thin laminae of phosphate with calcite and dolomite. (Pl. VI, Fig. 2). Apatite grains in general contain inclusions of quartz, magnetite and muscovite (Pl. VI, Fig. 3). Rhythmic alternate layers of apatite and carbonate are also observed in some of the samples.

CALCITE AND DOLOMITE :

Calcite and dolomite are the dominant gangue minerals of these stromatolitic phosphorites. They are fine to medium grained (Pl. VI, Fig. 1). The calcite grain varies from 0.2 to 1.2 mm in size whereas dolomite ranges in size between 0.3 to 1.4 mm. Fine to medium grained calcite and dolomite envelop the collophane, found in the intercolumnar space of the stromatolites (Pl. VI, Fig. 4). In some of the cases the penetration of the collophane grain boundaries into that of calcite clearly indicate the replacement of calcite by collophane possibly grain by grain. (Pl. VII, Fig. 2).

QUARTZ

Quartz in these phosphorites occur as subangular to subrounded grains with a diameter of about 0.009 to 0.3mm. The mineral shows oblique to slightly undulose extinction and occur as tiny inclusions in collophane, measureable in micron scale as well as coarse grained recrystallised quartz, often coated with ferruginous matter (Pl. IV, Fig. 1).

ACCESSORY MINERALS

The carbonate mosaic is constituted mainly of carbonte minerals together with minor amounts of feldspar, muscovite, biotite, sericite and a few crystals of tremolite.

Sericite and muscovite are generally colourless to pale green in colour. Muscovite occurs as disseminated laths where as sericite occurs as minute shred (Pl. IV, Fig. 2). Secondary limonite and limonitised pyrite occurs sporadically in studied phosphorite. The presence of limonite and altered pyrite indicates the oxidative alteration. Tremolite, light green in colour, can been seen in the argillaceous bands and appear as radiating tuft of tremolite and sericite (Pl. VII, Fig. 1). The ferruginous impurities are due to alteration, produced thin powdery coating of limonitic dust. Sericitisation is common in the dolomitic limestone of the area.

HEAVY MINERALS

The abundance and distribution of the heavy minerals are variable in the studied phosphorite and other associated rocks.In most of the phosphorites samples the amount of heavy minerals hardly excess 0.10 percent by number of the total grains in any

individual sample. Heavy minerals in these phosphorites includes mainly zircon, rutile, garnet, anatase, in order of their abundance. Small quantity of opaque minerals namely magnetite and ilmenite can also be seen in these phosphorite.

SCANNING ELECTRON MICROSCOPIC STUDY

Representative phosphorite samples from the Panchmahals areas were studied, using the HITACHI S-2300 scanning electron microscope. The present study indicate that the mineral apatite form the hexagonal prism and hexagonal pyramid (Pl,VIII, Fig.1). There are also obscure prisms and pyramids, altered and stripped, growing in the early stages of growth (Pl. VIII, Fig. 2).

Phosphorites is transvered invariably by the vein of recrystallized calcite in the criss cross fashion (Pl. VIII, Fig. 3). The growth of apatite grains in the calcite (Pl. IX, Fig. 1) indicate the replacement of calcite by apatite. The calcite and dolomite have hexagonal crystals (Pl. IX, Fig. 2) in which the sericitisation is common (Pl. IX, Fig. 3).

INFRA RED ABSORPTION SPECTRAL STUDY

The infra red spectra of three phosphorite samples recorded between 2.0μ and 15μ wavelength (550-1800 cm-1 frequency region) are reproduced in Fig. 5 and the frequencies with their classification regarding $(PO_4)^{-3}$) and $(CO_3)^{-2}$ ions are tabulated and are given in Table III and Table IV respectively.

The carbonate varieties of apatite give a broad absorption

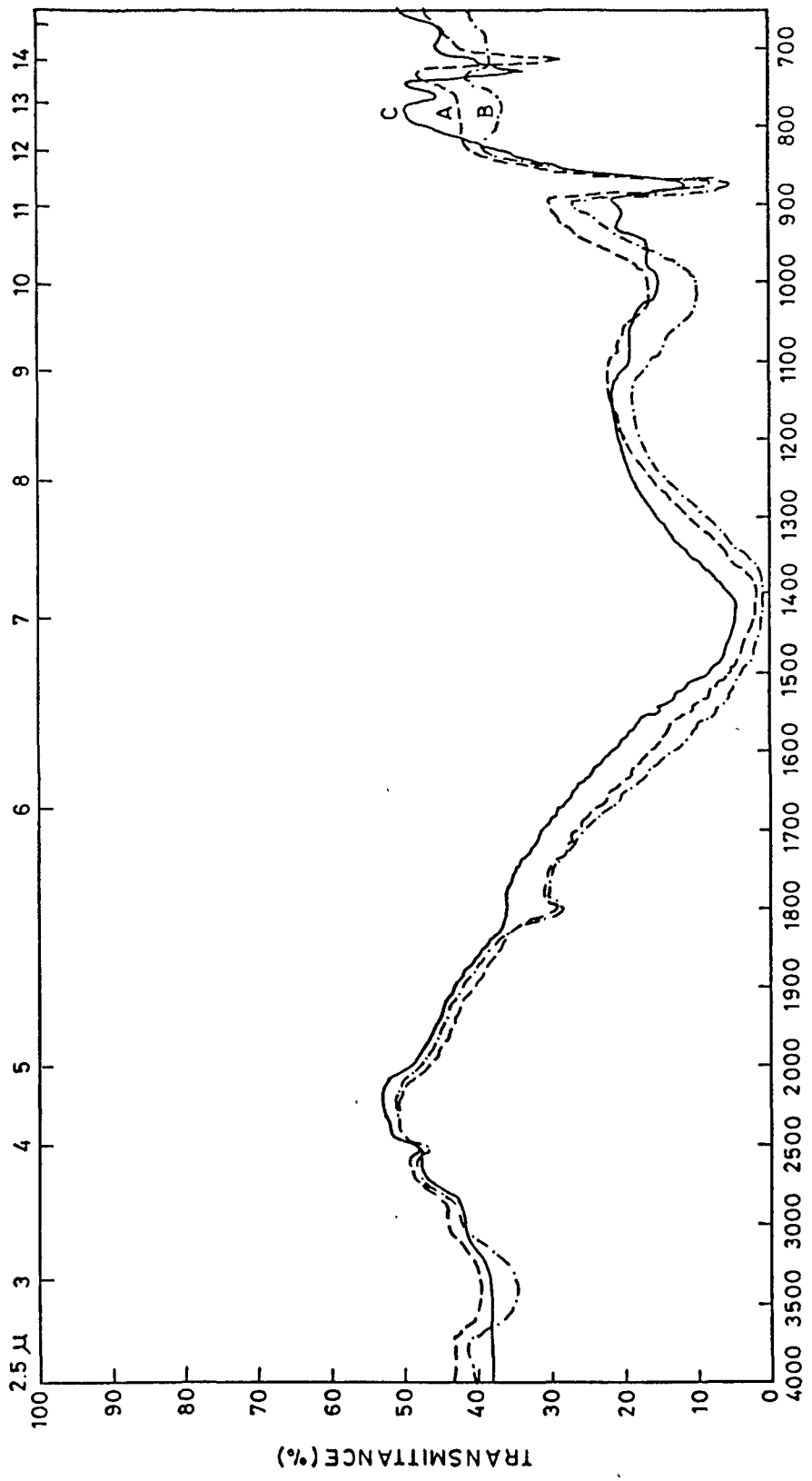


Fig. 5: Infra red spectra of Panchmahals phosphorites. A) Gandhra, B) Ranjitpura and C) Ambapani.

band at 104 cm^{-1} (9.6μ) with two satellite peaks at about 1100 cm^{-1} (9.15) and 960 cm^{-1} (10.4μ) frequency region. According to Adler, H.H. (1964), the peaks at 1100 cm^{-1} represent the V_3 mode (P.O asymmetric mode) while the peak at 960cm^{-1} correponds to V_1 (P-O-symmetric stretch) of PO^4 ions. On the other hand all the carbonate bearing apatite shows the characteristic peaks in 7μ region at approximately 1460 cm^{-1} and 1430 cm^{-1} frequencies which are absent in non-carbonate varieties. Additional small peaks are also present at 870 cm^{-1} frequency (11.5μ) in carbonate bearing apatite. The presence of (OH)in the apatite structure is shown by the presence of broad absorption band at 3500-3600 cm^{-1} (Romo, L.A. 1954) while the occasional presence of bands at about 1600 cm^{-1} is attributed to the presence of absorbed water molecules. (Adrievaskaya, N.F. et al., 1967).

Infra red spectral studies of the Panchmahals phosphorite (Fig.5) indicates a broad absorption band at 1450 cm^{-1} frequency region, and a very sharp peak in the 870 cm^{-1} frequency region, indicates the presence of carbonate bearing apatite. The V_4 vibration of carbonate ions in the 710 cm^{-1} indicate the presence of carbonate minerals i.e. calcite and magnesite (Possner, A.S. and Duckaerts, G. 1954). The broad peak in the 3400-3600 cm^{-1} frequency region indicates the presence of (OH) in the apatite structure. The weak bands at 770 cm^{-1} and 690 cm^{-1} frequency region in sample indicates the presence of quartz (Hunt, J.M. and Turner, D.S. 1953).

DOLOMITIC LIMESTONE

In general, the rocks is fine to coarse grained, poorly bedded and often containing argillaceous, siliceous or manganiferous impurities in varying proportion. Quartz and ferruginous vein are widespread. The major mineral constitutents of the dolomitic limestone includes mainly calcite and dolomite with quartz and opaques of iron (Pl. VI, Fig. 3). Calcite and dolomite were distinguished by staining with alizarin red-S (Friedman, G.M. 1959). Calcite grains generally range from 0.45 to 1.10 mm in diameter whereas the dolomite grains ranges between 0.3 and 1.40 mm in diameter. The quartz which is associated with dolomitic limestone occur as rounded to subrounded grains. Light green tremolite is developed in some of the layers and the more argillaceous bands show radiating tuffs of tremolite and sericite (Pl. V, Fig. 1). The ferruginous impurities by alternation and leaching have yellowish to brownish or reddish brown limonitic dust.

QUARTZITES

The overlying quartzite is well bedded, massive and crystalline . It is mainly composed of quartz with minor amounts of iron oxides and manganifereous impurities. The texture is typically granoblastic with ferruginous matter (Pl. V, Fig. 2). Fine inclusions of apatite and micaceous minerals are also present in this quartzite. The quartzite shows the sedimentary structures i.e. cross bedding and ripple marks.

PHYLLITES

Chlorite-quartz-sericite to chlorite-biotite bearing phyllites were identified in the area of interest. Microscopic studies of these phyllites indicate that fine to medium grained quartz, mica, boitite, fedspar, chlorite and sericite are the principal constituents with appreciable amount of carbonaceous materials. The other minor minerals identified include garnet, rutile and opaques of iron oxides.

Chapter-VI

GEOCHEMISTRY AND DISTRIBUTION OF MAJOR OXIDES

Fifty eight representative samples of phosphorite and the associated rocks i.e. dolomitic limestone, quartzites and phyllites from the Panchmahals district, Gujarat (Fig. 2) were subjected to chemical analysis for the quantitative determination of their major oxides viz., SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, Cao, MgO, P_2O_5, FeO, Na_2O, K_2O, H_2O^+, CO_2 and F by weight percent. The analytical results are presented in Tables V to VIII and discussed on the following lines :

i) Statement regarding the abundance and distributional trends of each of the major oxide determined in phosphorites and other associated rocks.

ii) The quantitative variation trends of the significant oxides in the phosphorites and their mutual relationship.

The statistical treatment of the geochemical data of Panchmahals phosphorite was carried out in order to determine their range of variation, mean, standard deviation and frequency percent distribution (Table IX). The relative distribution of the major oxides in quartzite, dolomitic limestone and phyllite is given in Table X.

MAJOR OXIDES

Silica (SiO_2)

The concentration of SiO_2 in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites vary from 7.83 to 11.31 percent, 2.7 to

10.4 percent, 5.68 to 10.81 percent and 4.32 to 10.11 percent respectively. The abundance of SiO_2 in dolomitic limestone, quartzite and phyllites is given in Table X.

The frequency polygon (Fig. 6) represents the mean values of SiO_2 ranging from 6.39 to 9.28 percent in phosphorite deposits of Chalvad, Gandhra, Ambapani and Ranjitpura. The frequency percent distribution (Fig. 7) showing unimodal nature of SiO_2 in Chalvad, Ambapani and Ranjitpura deposits but bimodal in Gandhra phosphorite deposit. The maxima are at 8 to 10 percent in Chalvad, 2 to 4 and 6 to 8 percent in Gandhra, 6 to 8 percent in Ambapani and 4 to 5.5 percent in Ranjitpura.

Alumina (Al_2O_3)

The Al_2O_3 content in the phosphorites of Chalvad, Gandhra, Ambapani and Ranjitpura ranges from traces to 1.43 percent, 0.98 to 1.56 percent, 0.89 to 1.41 percent and traces to 1.58 percent respectively as shown in table IX. The concentration of Al_2O_3 in dolomitic limestone varies from 0.78 to 1.21 percent, in quartzite 2.11 to 2.88 percent and in phyllite it is 12.98 to 14.86 percent as shown in table X.

The mean values of Al_2O_3 in these phosphorites vary from 1.12 to 1.34 percent (Fig. 6). The frequency percent distribution shows bimodal nature of alumina in Chalvad and Ambapani whereas unimodal in phosphorite deposits of Gandhra and Ranjitpura. The maxima are 1.2 to 1.6 percent in case of Chalvad, 1.3 to 1.5 percent in Gandhra, 0.9 to 1.1 percent and 1.3 to 1.5 percent in Ambapani and 1.2 to 1.6 percent in Ranjitpura phosphorite.

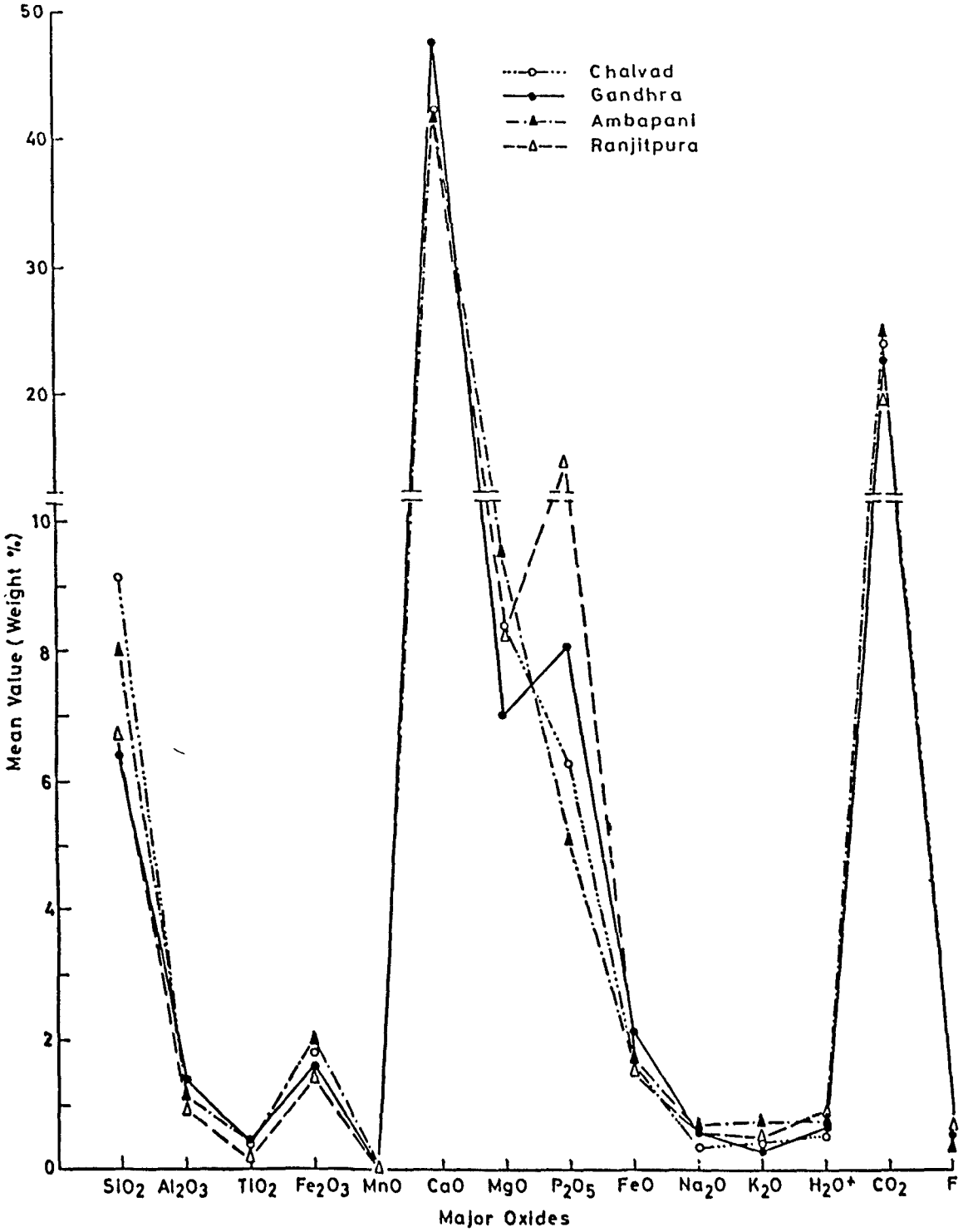


Fig. 6: Mean values (Weight%) of major oxides in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites.

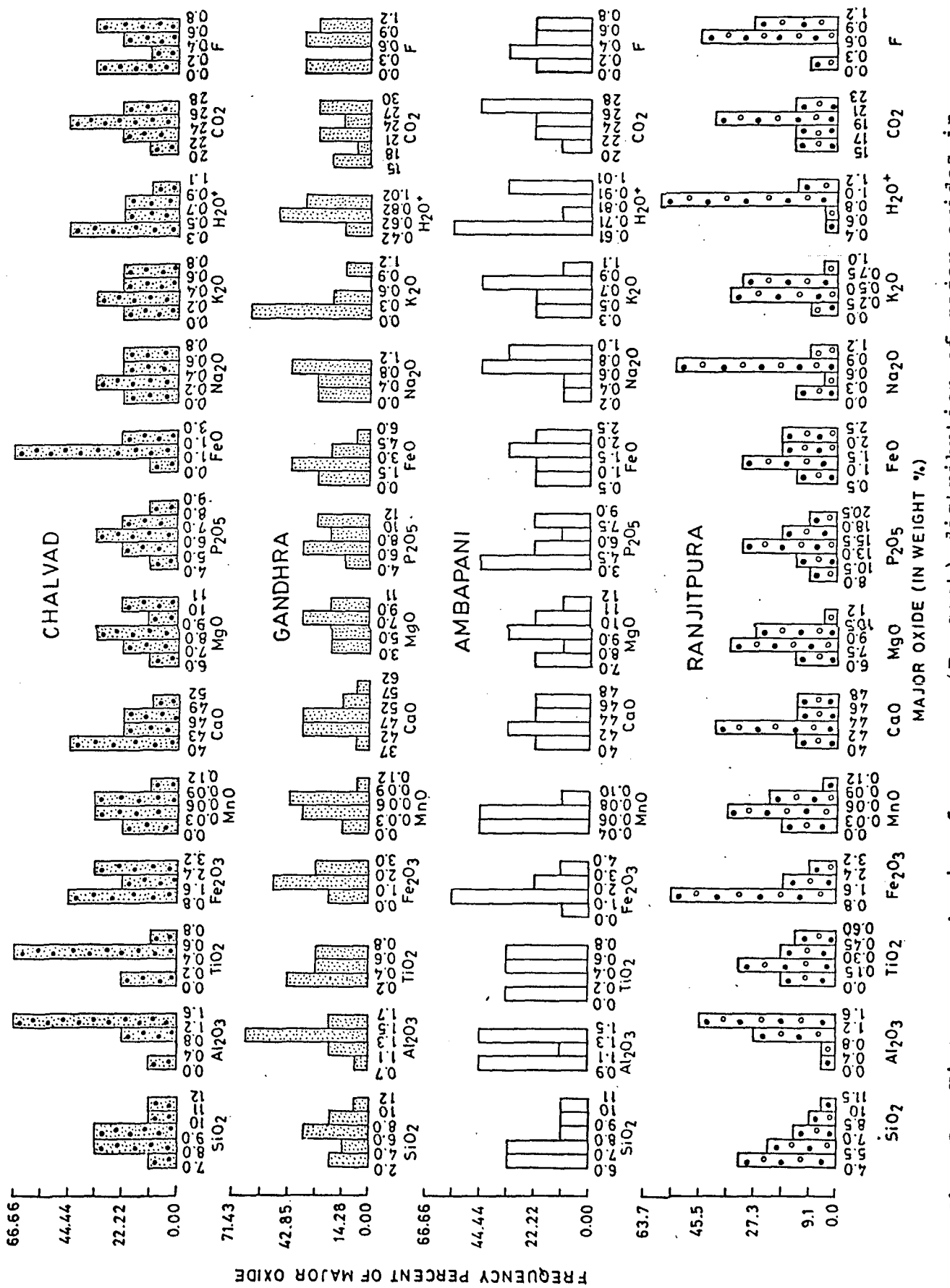


Fig. 7: Histograms showing frequency (Percent) distribution of major oxides in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites.

Titania (TiO_2)

The concentration of TiO_2 in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites ranges from traces to 0.67 percent, 0.27 to 0.8 percent, traces to 0.64 percent and traces to 0.60 percent respectively. The abundance of TiO_2 in dolomitic limestone, quartzite and phyllite varies from traces to 0.21 percent, traces to 0.23 percent and 0.43 to 0.91 percent respectively.

The average value of the TiO_2 in these phosphorites vary from 0.26 to 0.47 percent (Fig. 6). The frequency percent distribution showing unimodal nature of TiO_2 in phosphorites deposits of Gandhra and Ranjitpura whereas the bimodal nature of Chalvad and Ambapani deposits. The maxima of TiO_2 percent in Chalvad, Gandhra and Ranjitpura are at 0.4 to 0.6 percent, 0.2 to 0.4 percent and 0.15 to 0.3 percent respectively.

Ferric Oxide (Fe_2O_3)

Fe_2O_3 content in the phosphorite of Chalvad varies from 0.98 to 3.02 percent with mean value of 1.82 percent, in Gandhra from 0.58 to 2.99 percent with an average of 1.58 percent, in Ambapani from 0.79 to 3.41 percent with an average of 1.58 percent, in Ambapani from 0.79 to 3.41 percent with an average of 1.99 percent and in Ranjitpura the Fe_2O_3 content varies from 0.86 to 3.01 with the mean value of 1.50 percent. Thus it is clear that the mean values vary from 1.50 to 1.99 percent in these phosphorites (Fig. 6).

The frequency percent distribution (Fig. 7) showing unimodal nature of Fe_2O_3 in phosphorites of Gandhra, Ambapani and Ranjitpura whereas it is bimodal in Chalvad phosphorites. The

maxima are at 0.8 to 1.6 percent in Chalvad and Ranjitpura and 0.1 to 2.0 percent in Gandhra and Ambapani phosphorites. The abundance of Fe_2O_3 in samples of dolomitic limestones, quartzite and phyllite vary from 0.98 to 1.87 percent, 3.26 to 4.07 percent and 3.92 to 4.44 percent respectively (Table X).

Manganese Oxide (MnO)

MnO content in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites varies from traces to 0.11 percent, 0.02 to 0.12 percent, 0.04 to 0.09 percent and traces to 0.10 percent respectively. The abundance of MnO in dolomitic limestone, quartzite and phyllite vary from 0.06 to 0.11 percent, 0.06 to 0.14 percent, 0.11 to 0.17 percent respectively.

The study of frequency percent histograms (Fig. 7) indicate unimodal distribution of MnO in these phosphorites. The maxima of MnO are at 0.03 to 0.09 percent in Chalvad, 0.06 to 0.09 percent in Gandhra, 0.04 to 0.08 percent in Ambapani and 0.3 to 0.06 percent in Ranjitpura phosphorites. The average value of MnO in these phosphorites ranges from traces to 0.12 percent (Fig. 6).

Lime (CaO)

The variation trends of CaO in phosphorites of Chalvad, Gandhra, Ambapani and Ranjitpura ranges from 40.36 to 49.31 percent, 37.76 to 58.19 percent, 40.32 to 47.81 percent and 10.70 to 47.12 percent respectively. CaO in dolomitic limestone, quartzite and phyllites ranges from 40.51 to 43.00 percent, 2.89 to 3.81 percent and 2.79 to 3.45 percent respectively.

The frequency percent histograms indicate unimodal

distribution of CaO in these phosphorites. The maxima are at 40 to 43 percent in Chalvad, 42 to 52 percent in Gandhra, 42 to 44 percent in Ambapani and 42 to 44 percent in Ranjitpura phosphorites. The mean value of CaO in these phosphorites ranges between 43.57 and 47.54 percent (Fig. 6).

Magnesia (MgO)

The quantitative variation trends of MgO in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites vary from 7 to 11 percent, 3.15 to 10.89 percent, 7.81 to 11.90 percent and 6.94 to 11.08 percent respectively. MgO in dolomitic limestone, quartzite and phyllites ranges from 7.48 to 9.00 percent, 1.02 to 1.12 percent and 2.40 to 2.72 percent respectively (Table X).

The frequency percent distribution of MgO is bimodal in Chalvad and Ambapani phosphorites whereas unimodal in Gandhra and Ranjitpura phosphorites. The maxima are at 8 to 9 percent in Gandhra, 7 to 8 and 9 to 10 percent in Ambapani and 7.5 to 9 percent in Ranjitpura phosphorite. The average value of MgO in these phosphorites ranges from 7.02 to 9.55 percent (Table IX).

Phosphorous pentaoxide (P_2O_5)

The variation trends of P_2O_5 in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites ranges from 4.8 to 8.9 percent, 5.26 to 11.78 percent, 3.89 to 8.62 percent and 8.78 to 20.11 percent respectively. The abundance of P_2O_5 in dolomitic limestone, quartzite and phyllite ranges from 0.04 to 0.41 percent, 0.08 to 0.50 percent and traces to 0.21 percent respectively.

The mean value of P_2O_5 in the studied phosphorites vary from 5.65 to 14.38 percent (Fig. 6). The frequency percent histograms

of P_2O_5 (Fig. 7) indicate unimodal symmetrical distribution of P_2O_5 in Chalvad and Ranjitpura areas whereas unimodal asymmetrical in Gandhra and Ambapani areas. The maxima is at 6 to 7 percent in Chalvad, 6 to 8 percent in Gandhra, 3 to 4 percent in Ambapani and 13 to 15.5 percent in Ranjitpura phosphorites.

Ferrous Oxide (FeO)

FeO content in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites vary from 0.89 to 2.6 percent, 0.12 to 4.76 percent, 0.81 to 2.21 percent and 0.82 to 2.37 percent with an average value of 1.64 percent, 2.23 percent, 1.52 percent and 1.52 percent respectively. The abundance of FeO in dolomitic limestone, quartzites and phyllites vary from 1.01 to 1.70 percent, 1.68 to 2.52 percent and 1.54 to 2.71 percent respectively.

The frequency distribution indicate unimodal nature of FeO in these phosphorites. The maxima is at 1 to 2 percent in Chalvad, 1.5 to 3 percent in Gandhra, 1.5 to 2 percent in Ambapani and 1 to 1.5 percent in Ranjitpura deposits.

Soda (Na_2O)

The variation trends of Na_2O in the phosphorites of Chalvad, Gandhra, Ambapani and Ranjitpura range from traces to 0.69 percent, 0.22 to 1.16 percent, 0.26 to 1.00 percent and 0.19 to 0.93 percent with an average value of 0.38 percent, 0.64 percent, 0.69 percent and 0.65 percent respectively (Table IX). The abundance of Na_2O in associated rocks viz. dolomitic limestone, quartzites and phyllite ranges from traces to 0.21 percent, 0.26

to 0.43 percent and 0.41 to 0.62 percent respectively.

The frequency percent distribution shows unimodal nature of Na_2O in these phosphorites. The maxima is at 0.2 to 0.4 percent in Chalvad, 0.8 to 1.2 percent in Gandhra, 0.6 to 0.8 percent in Ambapani and 0.6 to 0.9 percent in Ranjitpura phosphorites.

Potash (K_2O)

The variation trends of K_2O in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites are from traces to 0.80 percent, 0.04 to 1.02 percent, 0.31 to 1.10 percent and 0.19 to 0.93 percent with an average value of 0.40 percent, 0.34 percent, 0.71 percent and 0.46 percent respectively (Table IX). The abundance of K_2O in dolomitic limestone, quartzites and phyllites vary from traces to 0.16 percent, 0.29 to 0.39 percent and 1.11 to 1.96 percent respectively (Table X).

The frequency percent distribution of K_2O shows unimodal negatively skewed nature in Chalvad, Gandhra and Ranjitpura phosphorites (Fig. 7). The maxima are at 0.2 to 0.4 percent in Chalvad, traces to 0.3 percent in Gandhra, 0.7 to 0.9 percent in Ambapani and 0.25 to 0.5 percent in Ranjitpura phosphorites.

Loss on ignition (H_2O^+)

The variation trends of H_2O^+ in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites ranges from 0.39 to 0.91 percent, 0.42 to 1.01 percent, 0.61 to 1.01 percent and 0.41 to 1.20 percent. The mean value of H_2O^+ in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites is 0.61 percent, 0.73 percent, 0.76 percent, 0.94 percent respectively (Table IX). The abundance of H_2O^+ in dolomitic limestone, quartzites and phyllites varies from

0.2 to 0.34 percent, 0.5 to 0.86 percent and 4.48 to 5.08 percent respectively (Table X).

The study of frequency distribution of H_2O^+ indicate unimodal negatively skewed nature in Chalvad, Gandhra and Ambapani whereas unimodal positively skewed nature in Ranjitpura phosphorites. The maxima are at 0.3 to 0.5 percent in Chalvad, 0.62 to 0.82 percent in Gandhra, 0.61 to 0.71 in Ambapani and 0.8 to 1.0 in Ranjitpura phosphorites.

Carbon dioxide (CO_2)

The variation trends of CO_2 in phosphorites of Chalvad, Gandhra, Ambapani and Ranjitpura vary from 21.30 to 27.00 percent, 15.51 to 29.41 percent 21.83 to 27.90 percent and 15.13 to 22.50 percent respectively with an average value between 19.48 percent (in Ranjitpura phosphorites) and 25.16 percent (in Ambapani phosphorites) as shown in Fig. 6. The abundance of CO_2 in dolomitic limestone, quartzite and phyllite ranges between 39.60 to 41.44 percent, 0.68 to 1.18 percent and 9.02 to 10.33 percent respectively (Table X).

The frequency percent distribution histograms (Fig. 7) of CO_2 indicate unimodal symmetrical nature in Chalvad, bimodal nature in Gandhra and unimodal positively skewed nature in Ambapani and Ranjitpura phosphorites. The maxima are at 24 to 26 percent in Chalvad, 21 to 24 percent and 27 to 30 percent in Gandhra, 26 to 28 percent in Ambapani and 19 to 21 percent in Ranjitpura phosphorites.

Fluorine (F)

F content in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites varies from traces to 0.70 percent, traces to 1.10 percent, traces to 0.80 percent and traces to 1.02 percent with an average value of 0.36 percent, 0.58 percent, 0.36 percent and 0.76 percent respectively. The abundance of F in dolomitic limestone ranges between traces and 0.12 percent whereas fluorine is absent in quartzites and phyllites.

The study of frequency distributions (Fig. 7) indicate bimodal nature of F in Chalvad and Gandhra phosphorites whereas unimodal negatively skewed in Ambapani and unimodal positively skewed in Ranjitpura phosphorites. The maxima are at traces to 0.2 percent and 0.6 to 0.8 percent in Chalvad, traces to 0.3 percent and 0.6 to 0.9 percent in Gandhra, 0.2 to 0.4 percent in Ambapani and 0.6 to 0.9 percent in Ranjitpura phosphorites.

CHEMICAL COMPOSITION AND MUTUAL RELATIONSHIP OF SIGNIFICANT OXIDES

In order to understand the compositional characteristics and mutual relationship of significant oxides, the correlation coefficient among the major oxides (Tables XXXV to XXXVIII) and concentration plots of P_2O_5, and other importants oxides were attempted (Figs. 8 and 9) and discussed as follows:

CHEMICAL COMPOSITION

The results of the chemical analyses reveal that phosphorite deposits of Chalvad, Gandhra, Ambapani and Ranjitpura

are characterised by the presence of low to moderate concentration of Fe_2O_3, FeO and SiO_2, low concentration of Al_2O_3, TiO_2, MnO, Na_2O, K_2O, H_2O^+ and F and higher concentration of CaO, MgO and CO_2. The phosphorites of Ambapani are of very low grade, having an average concentration of P_2O_5 to about 5.65 percent whereas the phosphorites of Ranjitpura area are of medium grade with an average value of P_2O_5 to about 14.38 percent.

The apatite are generally named according to the relative proportion of F, Cl, OH, and CO_2 in the unit cell. McConnell (1938) restricted the term fluorapatite having less than one percent each of CO_2 and H_2O and more than three percent of fluorine. The chemical nature of apatite is considered to be complex and a wide variation in composition is known. Minerals of the apatite series have the general formula $Ca_{10}(PO_4)_6(F, OH, Cl)_2$. The chemical analysis shows the presence of SiO_2, Fe_2O_3 and MnO in appreciable amount which seems to be due to inclusion of quartz, secondary silicification and iron oxide coatings on phosphate minerals.

MUTUAL RELATIONSHIP OF SIGNIFICANT OXIDES

The geochemical behaviour of different elements and their mutual correlation has an important bearing on the origin of the phosphorites. The results of major elements analyses of phosphorites and associated rocks are presented in tables V to X and the variation trends of various oxides are plotted and given in tables XXXV to XXXVIII and illustrated in Fig. 6.

In order to understand the chemical nature and formational reactions of P_2O_5, attempt has been made to establish the relationship of P_2O_5 with other major oxides and discussed as follows:

P_2O_5 and CaO content of various phosphorite deposits exhibit a strong negative relationship with SiO_2 (Fig. 8-A). An antipathetic relationship also exists when SiO_2 is correlated with CaO, Na_2O and F (Tables XXXV to XXXVIII). It, therefore appears that much of SiO_2 content is not related to apatite. High SiO_2/Al_2O_3 ratios (Tables XI to XIV) and sympathetic relationship of SiO_2 with Al_2O_3, K_2O and Fe_2O_3 (Tables XXXV to XXXVIII) favours the coexistence of quartz and alumino-silicate minerals in these phosphorites.

The relationship of Al_2O_3 with P_2O_5 (Fig. 8-B) and CaO is antipathetic. The ability of alumina, which is closely associated with silica, to substitute Ca as well as P in significant amount is in confirmity to the recent extension of the possibilities of their isomorphic substitution as proposed by Fisher, D.J and McConnell (1969). The sympathetic relationship of Al_2O_3 with Fe_2O_3, MgO and K_2O (Figs. 9-C, G and D) suggests that alumina is partitioned element between alumino-silicate and carbonate fluorapatite minerals. The K_2O/Al_2O_3 ratio (Tables XI to XIV) indicates that potassium is contained in the alumino-silicate mineral phase.

Titanium is antipathetically related with P_2O_5 (Fig. 8-C) and CaO but it is sympathetically related with Fe_2O_3 and CO_2 (Tables XXXVI to XXXVIII) which suggest a closer association of

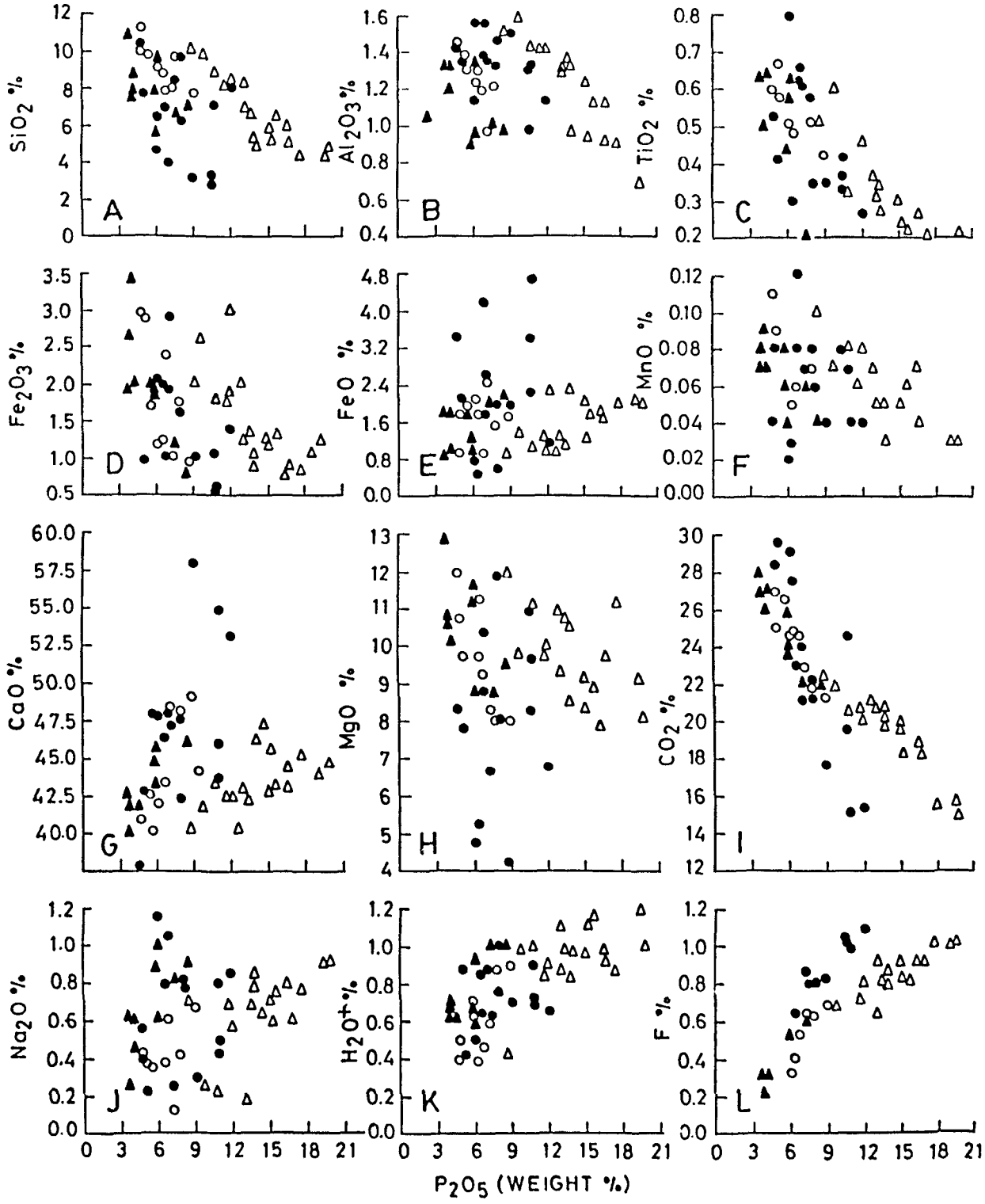


Fig. 8: Relationship of P_2O_5 with SiO_2, Al_2O_3, TiO_2, Fe_2O_3, FeO, MnO, CaO, MgO, CO_2, Na_2O, H_2O and F in Chalvad (○), Gandhra (●), Ambapani (▲) and Ranjitpura (△) phosphorites.

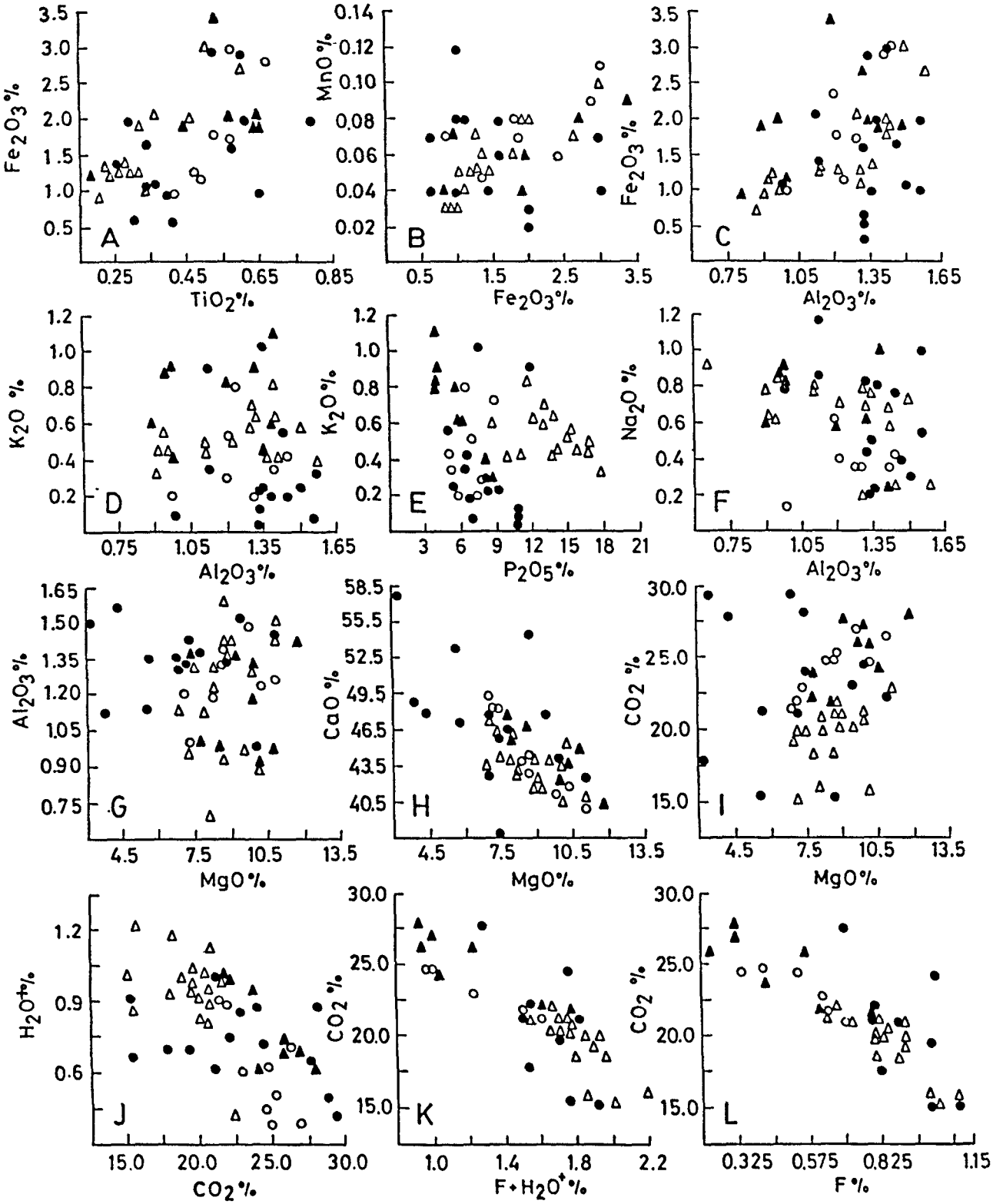


Fig. 9: Plots of Fe_2O_3-TiO_2, MnO-Fe_2O_3, Fe_2O_3-Al_2O_3, K_2O-Al_2O_3, K_2O-P_2O_5, Na_2O-Al_2O_3, Al_2O_3-MgO, CaO-MgO, CO_2-MgO, H_2O^+-CO_2, CO_2-$F+H_2O^+$ and CO_2-F in Chalvad (o), Gandhra (•), Ambapani (▲) and Ranjitpura (△), phosphorites.

Ti with Fe and C. This positive relationship of titanium with Fe and C indicate the presence of titaniferous magnesites. The nearly constant Al_2O_3/TiO_2 ratio (Tables XI to XIII) and sympathetic relationship of TiO_2 with Al_2O_3 suggests a closer association of Ti with Al which may be due to presence of nonopaque titanium minerals like rutile and anatase.

The antipathetic relationship of Fe_2O_3 with P_2O_5 (Fig. 8-D) and CaO indicates that iron oxide is not related to apatite. The existence of iron oxide as coating around the phosphate minerals may be due to oxidation of some admixed pyrite in the sediments. The Fe_2O_3/Al_2O_3 ratios indicate the association of Fe_2O_3 with alumino-silicate minerals. FeO is sypathetically related to MgO whereas Fe_2O_3 has negative relationship with magnesia (Table XXXVI) possibly due to replacement of Fe^{3+} by Mg^{2+} (Drever, J.J. 1971). Furthermore the lower Fe_2O_3/FeO values (Tables XI to XIV) in many of these phosphorite samples indicate the lower oxidation condition but the higher values in few of these samples indicate the increasing oxidation conditions. Thus the Fe_2O_3/FeO ratios suggest that these phosphorites were possibly precipitated under slightly reducing to fairly oxidizing conditions.

The plot and the correlation coefficient of MnO content against P_2O_5 indicate negative relationship (Fig. 8-F). The positive correlation of MnO with Fe_2O_3 possibly suggest the coprecipitation of Mn and Fe under fairly oxidizing conditions. The negative relationship of MnO with CaO and the variable MnO/CaO ratio (Tables XV to XVIII) may be attributed partly to

the substitution of Ca by Mn in calcite lattice on account of close similarity in the ionic radii of Mn^{2+} (0.80 A°) and Ca^{2+} (0.99 A°).

The strong positive correlation of P_2O_5 with CaO (Tables XXXV to XXXVIII) in these phosphorites suggest coprecipitation of lime and phosphate forming stable calcium phosphate under suitable pH condition. The CaO/P_2O_5 values (Tables XI to XIV) from geochemical data of phosphorites are virtually inconsistent and fall between 2.34 to 8.54 for these phosphorites which are higher than values of ideal fluorapatites (1.31). Such higher values of CaO/P_2O_5 ratios indicate that these phosphorites are composed of carbonate apatite formed as a result of replacement processes. Furthermore the CaO/P_2O_5 values increases with the increase of CO_2 content, possibly due to the substitution of PO_4 by CO_3. The presence of free carbonate and carbonate apatite is also supported by the ratio of CO_2/P_2O_5 which is very high (Tables XI to XIV).

Ames, L.L. Jr. (1959) observed experimentally that when calcite was exposed to alkaline solution at a pH of 7 or more with PO_4^{3+} concentration of one ppm or higher,it was replaced by carbonate apatite in a stable artificial aqueous phosphate and carbonate system to the probable formation of large marine phosphate deposits. Following Ames (1959) it seems possible that these phosphorites were formed as a result of the coprecipitation of carbonate and phosphates aided by simultaneous replacement of calcium carbonate by phosphate rich upwelling currents.

P_2O_5 and CaO exhibits strong negative relationship with MgO (Figs. 8-H). The presence of Mg^{2+} rather inhibits the growth of apatite crystallites, formed during regional metamorphism and reconstitution of phosphate minerals. Bachra, B.N. et al., (1965), Marten, C.S. and Harriss R.C. (1970) assumed that Mg^{2+} inhibits the precipitation of apatite and competes with Ca^{2+} sites in the apatite structure. However, Marten and Harriss (1970) also suggested that there was probably a threshold of Ca/Mg above which apatite could precipitate. The magnesium ion seems to retard the reaction (salinity) when Ca/Mg ratio approaches 4.5 to 5.2. The diagenetic reaction occurring within anoxic sediments could raise the Ca/Mg ratio to the point where apatite may precipitate. The replacement of magnesium calcite by carbonate apatite might be responsible for forming phosphatic dolomite (decrease in Ca/Mg ratios). Possibly Mg^{2+} ions are free from the calcite lattice in the process of reorganising constituent elements to form carbonate apatite. However, Ca^{2+} ions are readily taken in carbonate apatite structure with the rejection of Mg^{2+} ion. The higher Ca/Mg ratio in samples of Chalvad and Gandhra phosphorites indicates the entrance of Ca^{2+} ion in carbonate apatite structure, while low Ca/Mg ratio in samples of Ambapani and Ranjitpura phosphorites suggest the replacement of magnesium calcite by carbonate apatite. The positive correlation of MgO with Al_2O_3 in Chalvad and Ranjitpura phosphorites and the MgO/Al_2O_3 ratio (Tables XI to XIV) suggests that Mg is also included in the clay fraction.

The positive relationship of Na_2O with P_2O_5 (Fig. 8-J) and

high Na_2O content in these phosphorites indicate the formational environment of high salinity (Russell, R.T. and Trueman, N.A. 1971).

K_2O shows negative correlation with P_2O_5 and CaO of Ambapani and Ranjitpura phosphorites (Tables XXXVII and XXXVIII) whereas in Chalvad and Gandhra phosphorites K_2O shows insignificant relationship with P_2O_5 and CaO (Tables XXXV and XXXVI). The positive relationship of K_2O with Al_2O_3 (Tables XXXV, XXXVII and XXXVIII) is possibly due to the presence of potash feldspar in these phosphorites .

The concentration plots and correlation coefficient values of H_2O^+ with P_2O_5 and CaO shows a good positive relationship in the phosphorites of Chalvad, Ambapani and Ranjitpura area (Table XXXV, XXXVII, XXXVIII). The negative correlation of H_2O^+ with CO_2 (Tables XXXV to XXXVIII) and the high CO_2/H_2O ratio (Tables XI to XIV) indicate carbonate bearing hydroxyl apatite composition of phosphorites of some samples.

The results of the present investigation shows that the concentration of CO_2 content is too high to be explained as carbonate impurity. The explanation may be found in one or more of the following situations :

1. Particles of `Amorphous' calcite is too small to have coherent or ordered atomic structure (Thewlis, J. and others, 1939, Carlstrom, D. 1955).
2. Carbonate or bicarbonate ions are limited to the surface of apatite crystallite or exchanged with surface phosphate ions

(Newman, W.F. and Newman, M.W. 1953) and interstitial sites.

3. CO_3^{2-} substitution of Ca^{2+} or PO_4^{3-} in the apatite structure (Deans, T. and Vincent, H.C. G. 1938; Sandell, E.B. et al., 1939; McConnell, D. and Gruner, J.W. 1940; McConnell, 1952 and 1960).

4. Function of CO_3^{2-} radical in the apatite structure may be present as an integral part of the apatite lattice (Altuschuler, Z.S. et al., 1958; Rooney, T.P. and Kerr, P.F. 1967; McClellan, G.H. and Lehr, J.R. 1969).

Physiological chemists favour the hypothesis (1) and/or (2) for bone apatite, while the mineralogists generally prefer the hypothesis (3) and (4).

In an attempt to explain the substitution of CO_3 group for PO_4 group, McConnell (1973) suggested that the substitution might have taken place in the following manner:

(i) PO_4 -------> CO_3OH or CO_3F

(ii) H_2O^+ -------> Ca^{2+}

A strong negative correlation of CO_2 with P_2O_5 and CaO (Table XXXV to XXXVIII) suggest the substitution of both Ca and P by C. The positive correlation coefficient values of CO_2 with MgO (Tables XXXVI to XXXVIII) indicate that much of CO_2 is found associated with MgO. It, therefore, appear that CO_2 is more a function of magnesian carbonate.

The CO_2/P_2O_5 ratio (Tables XI to XIV) are higher than ideal fluorapatite, indicate the composition of carbonate apatite with the presence of free carbonate. Furthermore the higher CO_2/P_2O_5 ratio indicate the possibilities of PO_4^{3-} substitution by CO_3^{2-}.

The variable F/P_2O_5 and F/H_2O^+ ratio (Tables XI to XVIII) approach very near to carbonate apatite, carbonate hydroxyl fluorapatite and carbonate hydroxyl apatite.

The geochemical characteristics of the various constituents of these phosphorites are discussed in the light of appropriate triangular diagrams (Fig. 10) based on the analytical determinations. The bulk components are recalculated to 100 weight percent (Tables XIX to XXXIV) and discussed as follows:

The $CaO-MgO-P_2O_5$ diagram (Fig. 10-A) illustrates the variation trends of CaO and P_2O_5 with respect to MgO in the system. It demonstrates that with the addition of MgO there is pronounced decrease of P_2O_5 and CaO.

The $CaO-MgO-SiO_2$ diagram (Fig. 10-B) exhibits the increase of silica and magnesia with the decrease of lime. However, the low concentration of SiO_2 indicate that MgO is related to dolomitic limestone and magnesian silicate minerals.

In the Fig. 10-C, the system shows that MgO is sympathetically related to CO_2 while CaO increases with decreasing CO_2 and vice versa. The relative higher value of CO_2 with the increase of MgO may be a relative phenomena indicating a positive evidence for addition of these constituents in Panchamahals phosphorites, which might have undergone partial dolomitization as indicated by lower to medium values of CaO/MgO ratio (Tables XV to XVIII).

The plots $SiO_2-MgO/CaO-H_2O^+$ and $SiO_2-MgO/CaO-CO_2$ (Figs. 10-D and E) illustrate that CO_2 and H_2O^+ played an important role in

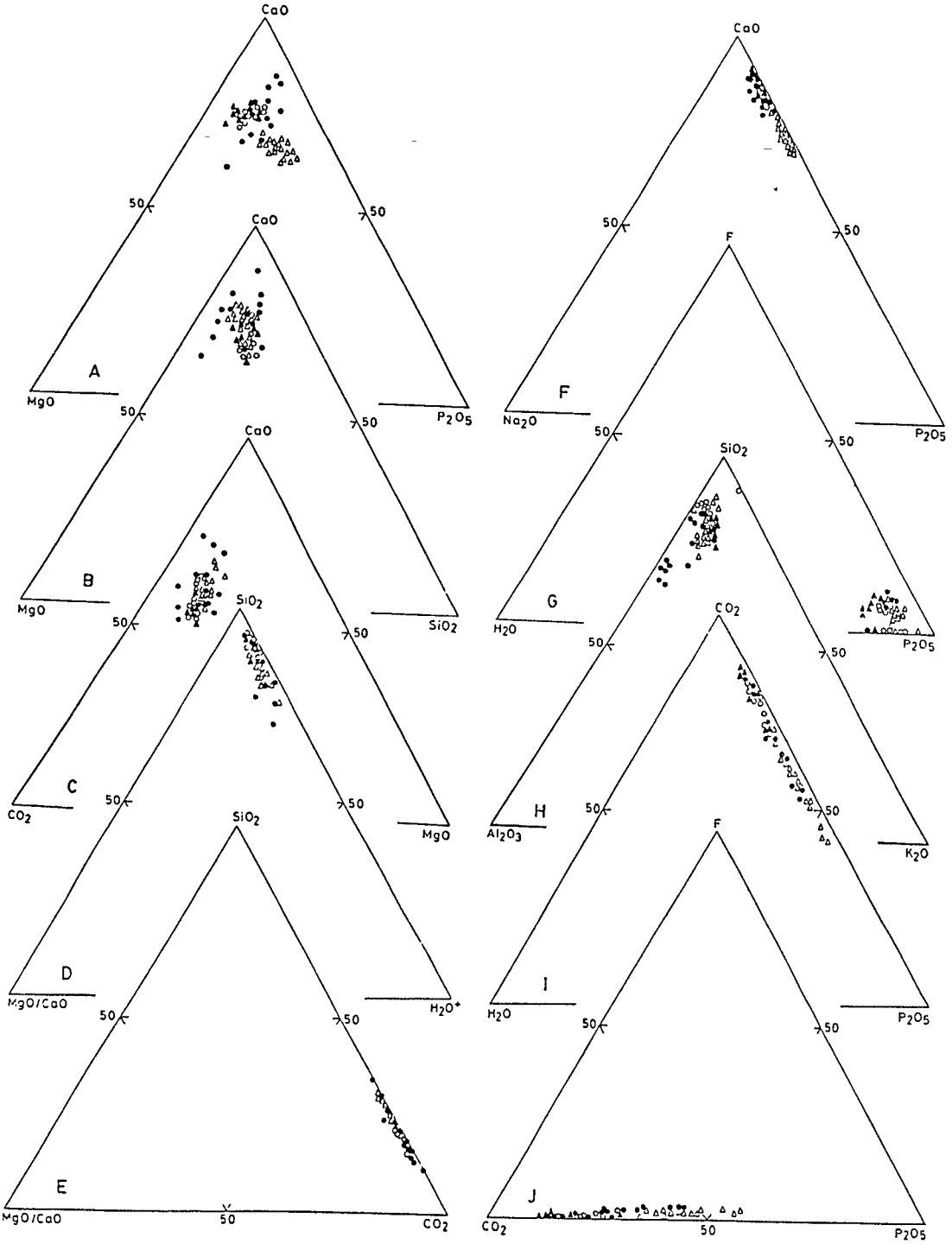


Fig. 10: Triangular diagrams showing compositional variations of major oxides of Chalvad (○), Gandhra (●), Ambapani (▲) and Ranjitpura (Δ) phosphorites.

formation of the phosphate minerals. It has been observed that SiO_2 follows the trend of MgO and H_2O^+ to some extent, possibly due to presence of hydrated magnesian silicate minerals, diluting CaO and P_2O_5. It may be observed that the samples having higher Ca/P+C ratio also have high H_2O^+ content and vice versa indicating the substitution of $(OH)_4$ for (PO_4).

The plot of Na_2O-CaO-P_2O_5 (Fig. 10-F) indicates that the constituents are related to carbonate apatite. The similar trend of Na_2O with respect to CaO and P_2O_5 may be interpreted as due to coupled substitution of Na^+ for Ca^+ and PO_4 to preserve electroneutrality as discussed by Rao, L.A.K. (1982).

The plots of P_2O_5-F-H_2O^+ and P_2O_5-F-CO_2 system (Fig. 10-G and J) indicate the variation trend of P_2O_5 with respect to CO_2+F and CO_2+H_2O. The excess of H_2O^+ and deficiency in F content of these phosphorite samples indicate the replacement of F by OH. It is logically concluded that (CO_3^{2-}) + F^{1-} substituted for PO_4^{3-} on the basis of one for one (P ==== C) as observed by Gulbrandsen, R.A. et al., (1966).

The P_2O_5-H_2O^+-CO_2 diagram (Fig. 10-I) indicates similar trends of substitution in the manner of PO_4--->CO_3OH as well as possibility of PO_4 === $(OH)_4$ substitution. Furthermore the increase of CO_2 and H_2O in most of the samples clearly indicate the presence of carbonate hydroxyl apatite.

The principal group of constituents not related to apatite composition are those forming quartz-silicate group of minerals. The plot K_2O-Al_2O_3-SiO_2 (Fig. 10-H) indicate that the potash also increases with increase of alumina at the expense of silica. The

low K_2O/Al_2O_3 and SiO_2/Al_2O_3 ratio reflect the insignificant amounts of admixed alumino-silicate minerals. Another significant features is the association of silica in substantial quantity with the other constituents.

Chapter VII

GEOCHEMISTRY AND DISTRIBUTION OF TRACE ELEMENTS

Trace elements study is not of recent origin. Earlier workers have emphasized the significance and distribution of trace elements. Washington, H.S. (1913) while discussing the distribution of the elements in the earth's crust stated that minor elements were related not only to the rock types but also to the major elements constituting the rocks.

Goldschimidts, V.M. (1937) proposed a geochemical classification on the basis of their chemical affinity. He observed that the elements indicate their presence into an iron phase, sulphide phase and a silicate phase and classified them into siderophile, chalcophile and lithophile respectively.

According to Goldschimidts (1954) concept of trace element geochemistry, there is a tendency of certain minor elements to follow major elements that are similar to that in radius and bond type. Ringwood, A.E. (1955) used electronegativity as an indicator of bond type in rocks. However, the concept of electronegativity was first advanced by Pauling, L. (1948,1960) and defined it as "the power of an atom in a molecule to attract an electron into itself". Ringwood (1955) applied electronegativity to the distribution of the trace elements and proposed the following rule :

"Whenever mutual replacement between two elements in a crystal is possible, possessing appreciably different electronegativity, the element with the lower electronegativity

will be preferentially incorporated because it forms a stronger and more ionic bond than the other". This rule satisfactorily applied to such cases in which the difference in electronegativity is more than one. Ringwood (1955) also favoured the use of ionisation potential as suggested earlier by Ahrens, L.H. (1953) and Goldschimidt (1954) as a possible replacement of electronegativity criteria.

Graf, D.L. (1960) noticed the following forms in which minor and trace elements occur in carbonates viz.,

i) Solid solubility in the individual mineral,

ii) in detrial mineral,

iii) as authigenic precipitates,

iv) as by products of recrystallization and

v) elements or their compounds adsorbed by the various minerals.

Strakhov, N.M. and his co workers (1959) mentioned that Fe, Mn, P and number of minor elements viz., Cu, Ni, Co, Zn, Pb, Cr, V and Ga remain mainly in suspension during transportation by river water and enter true solution only to a minor extent.

Intense chemical weathering of the source rock breaks down the complex silicates, alumino-silicates and sulphides of igneous and metamorphic rocks. The elements thus obtained Fe, Mn, P, V, Cr, Co, Cu, Pb, Bi etc. migrate partly in suspension as clay minerals, consequently there will be a higher concentration of the elements in fine grained argillaceous and calcareous deep water sediments. Although there are well established methods

dealing with the geochemical data of igneous rock. However, there is no general recognised procedure for interpretating the chemical variations in closely related series of sedimentary rocks. Krynine, P.D. (1948) pointed out that the sedimentary rocks may be regarded as a mixture of material carried out into the basin of deposition in the solid state and in solution. This concept has been applied in sedimentary geochemistry by Nicholls, G.D. (1958) and Nicholls and Loring, D.H. (1962).

For comparing the relative abundance of various trace elements in different rocks the following arbitrary scale of concentration of element has been adopted.

Value (ppm)	Scale symbol	Concentration
>300	E.H.	Exceptionally high
200-300	V.H.	Very high
100-200	H.	High
50-100	M.	Medium
10-50	L.	Lower
2-10	V.L.	Very low
0-2	Tr.	Traces
<0	N.D.	Not detectable

The most complete data about the geochemistry of phosphorites available were published by Gulbrandsen (1966). The average concentration of trace elements in phosphorite is also given by Krauskopf (1955), Prevot, L. and Lucas, J. (1979). The concentration of various trace elements, determined in the phosphorites of the study area have been compared with the average values determined in the phosphorites by Gulbrandsen

(1966), Prevot and Lucas (1979), Krauskopf (1955), Tooms, et al., (1969) and given in Table XLVIII.

The concentration of trace elements of phosphorites and associated rocks of the study area along with mean values are given in Tables XXXIX to XLIII. Their relative distribution has been shown in Figs. 11, 12 and 13 and discussed as follows:

Copper

Copper is a chalcophile element in its geochemical behaviour. It occurs mainly in sulphide state though small amount of copper has also been reported from silicate and carbonate phases. The similarities among the ionic radii of Cu^{2+}(0.71 A°), Fe^{2+}(0.75 A°) and Mg^{2+}(0.66 A°) make it possible for Cu^{2+} to replace Fe^{2+} as well as Mg^{2+} as for example in tourmaline (Carobbi, G. and Pieruccini, R. 1947).

Ringwood (1955) compared the electronegativity of Cu^{2+}(1.8) and Na^{+}(0.9) and pointed out that Cu^{2+} bond would be weaker as compared to the Na^{+}-O bond. Similarly in case of Cu^{2+}(2.0) and Fe^{2+}(1.65), the Cu-O bond would be weaker as compared to the Fe^{2+}-O bond.

It has been experimentally shown that Cu is effectively absorbed by $Fe(OH)_3$, $Mn(OH)_4$ and clay minerals (Krauskopf, 1956), and Synder, J.L. (1959) suggested the replacement of sodium and divergent iron in silicate and oxides by copper in the formation of sulphide minerals.

The analytical results indicate that the copper concentration is extremely low when compared with the threshold

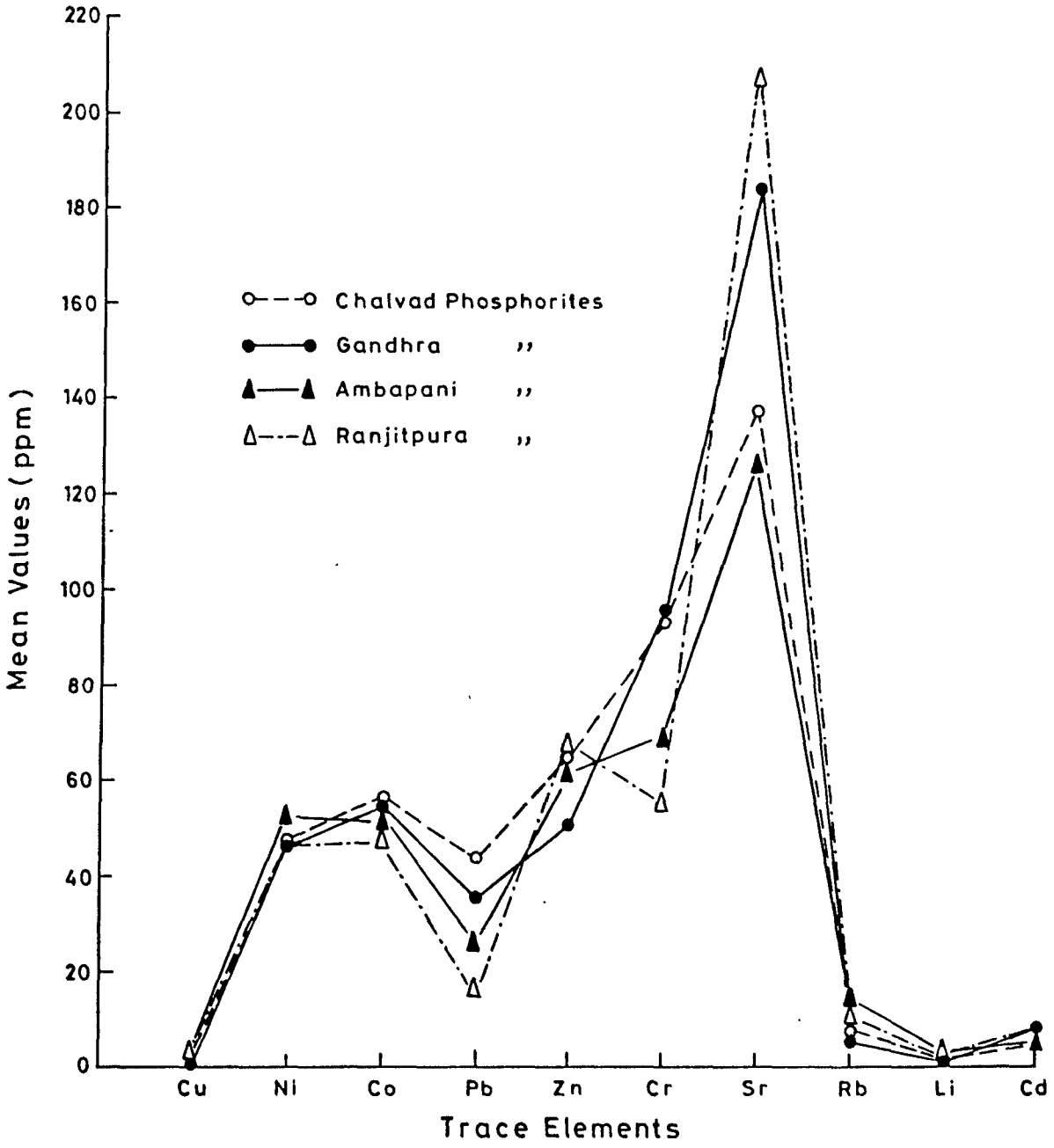


Fig. 11: Mean values (ppm) of various trace elements of Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites.

values for the phosphorites given by the Gulbrandsen (1966) and Prevot and Lucas (1979) as shown in Table XLVIII. The Cu content varies from n.d. to 7 ppm in Chalvad and Ambapani, n.d. to 6 ppm in Gandhra and n.d. to 8 ppm in Ranjitpura phosphorites. Copper content is negatively correlated with P_2O_5 of Panchmahals (Tables XXXV, XXXVI and XXXVIII). The negative relationship of Cu with P_2O_5 clearly indicate the ionic substitution of copper in apatite lattice during diagenesis. The negative relationship of Cu with FeO (Table XXXVI and XXXVIII) and MgO (Tables XXXV and XXXVII) may be due to the replacement of Fe^{2+} and Mg^{2+} by Cu as discussed by Carobbi and Pieruccini (1947).

The extremely low content of Cu is possibly due to the presence of algae as it is toxic for most of the life activities of the algal bodies. It seems possible that these algae were responsible for the removal of the Cu from the stromatolites and concentrated in the rocks adjacent to algal matter (Raha, P.K. 1978, Verma, K.K. 1978 and Rao, L.A.K. 1982).

Nickel

Geochemically, nickel is a siderophile element. The distribution of nickel in rocks was studied by Vogt, J.H.L. (1923). The bulk of Ni is always found associated with the metallic iron. The ionic radii of Ni^{2+}(0.69 A°) being very near to those of Mg^{2+}(0.66 A°) and Fe^{2+}(0.75 A°) should be able to replace one or both the elements in the rock. Goldschimidt (1944) suggested that Ni is likely to be enriched in the Mg-bearing minerals because Ni-O bond is stronger than Mg-O bond on account of its more covalent nature. But Ringwood (1955,56) suggested the

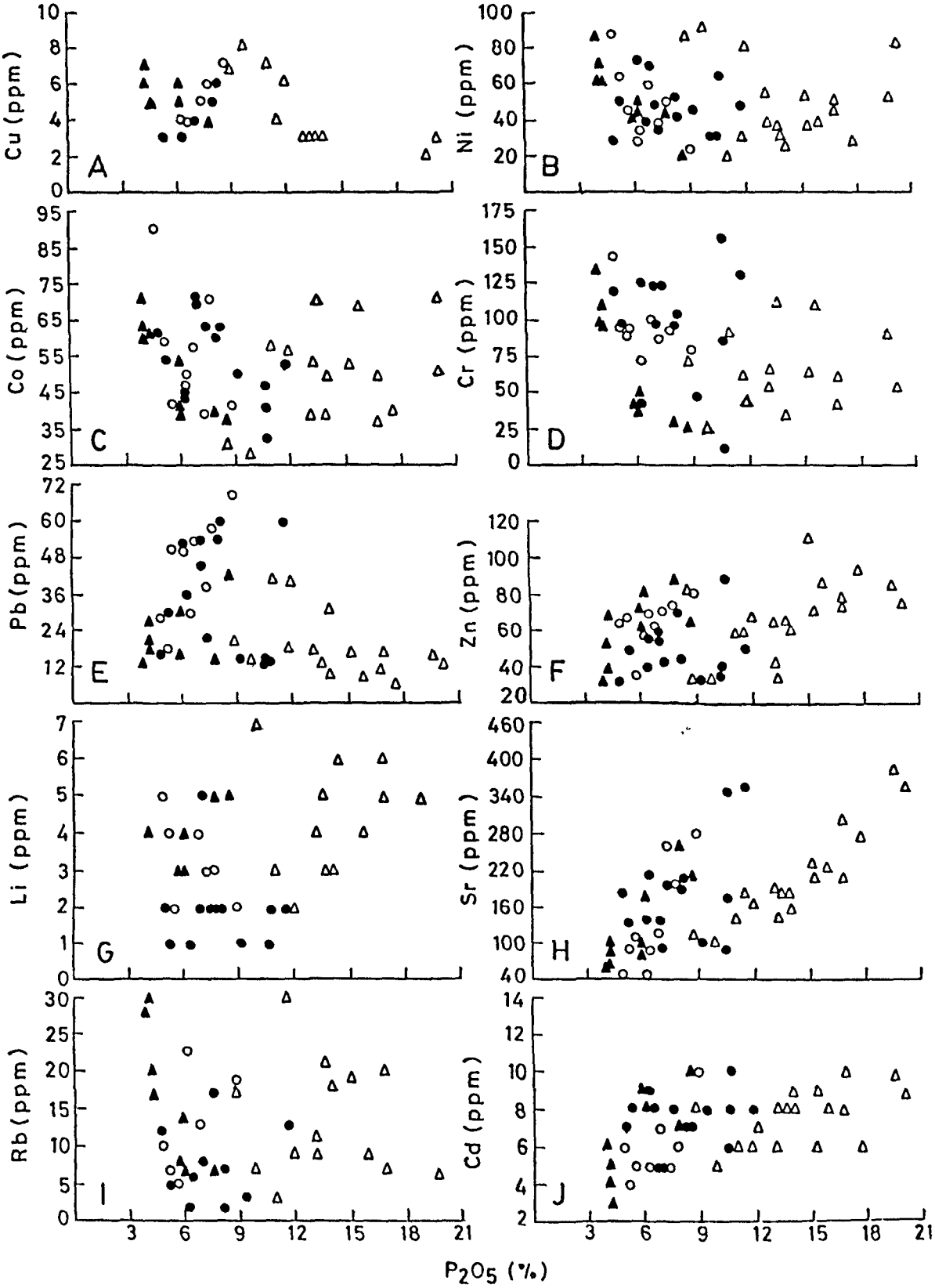


Fig. 12: Relationship of P_2O_5 with Cu, Ni, Co, Cr, Pb, Zn, Li, Sr, Rb and Cd in Chalvad (○), Ghandhra (●), Ambapani (▲) and Ranjitpura (△) phosphorites.

relationship among Mg-Ni-Fe phase on the basis of their electronegativity and stated that "the effect of increased covalent bonding is to weaken the bond". He pointed out that since the radius of Ni^{2+} is smaller than Fe^{2+} the former could substitute the latter and further Fe-O bonding is weaker than Ni-O bonding and Fe^{2+} is more mobile than Ni. This may render Fe^{2+} to be easily substituted by Ni^{2+}.

The concentration of nickel in carbonate rocks has been reported by many earlier workers, i.e. 3 to 10 ppm by Krauskopf (1956), 10 ppm by Runnels, R.T. and Schleicher, J.A. (1956), 15 ppm by Graf (1960) and 10 to 15 ppm by Turekian, K.K. and Wedepohl, K.H. (1961). The studies carried out by Krauskopf (1955), Gulbrandsen (1966) and Prevot and Lucas (1979) indicate that in phosphorites the concentration of Ni ranges from 4 to 20 ppm, 100 ppm and 21 to 64 ppm respectively.

The present study indicates the concentration of Ni ranges from 23 to 88 ppm in Chalvad, 28 to 72 ppm in Gandhra, 38 to 71 ppm in Ambapani and 25 to 91 ppm in Ranjitpura (Table XXXIX to XLII). This value is nearly in the range of the value as quoted by Prevot and Lucas (1979). The Ni levels in studied phosphorites are less than the values reported by Gulbrandsen (1966) and Krauskopf (1955). Ni shows negative relationship with P_2O_5 (Fig. 12-B) but a good positive relation with Fe_2O_3 (Table XXXV to XXXVIII). Further it is noted that Ni concentration increases when phosphorites contain iron oxides (Debrabant, P. and Paquet, J. 1975; Lucas et al., 1978).

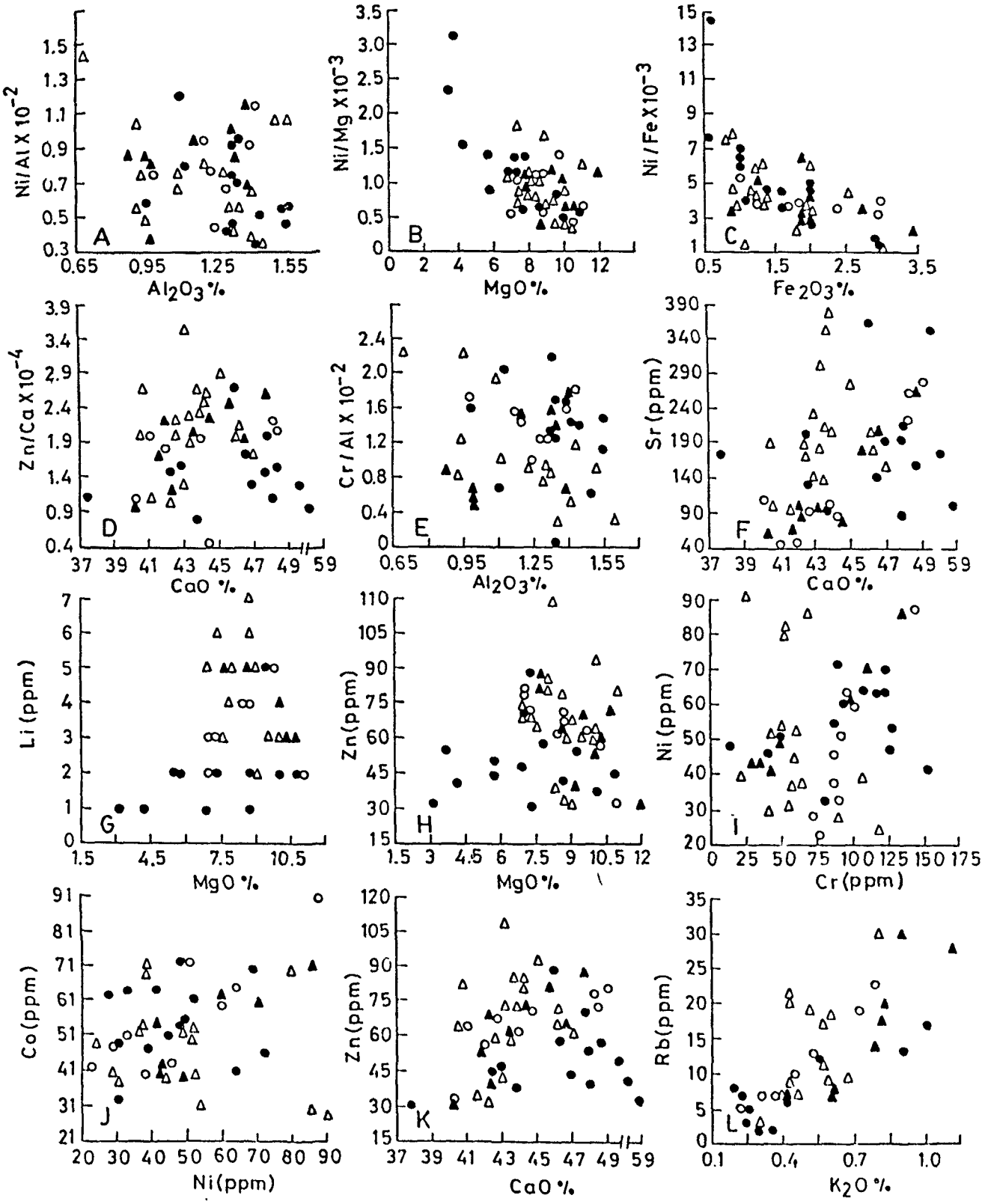


Fig. 13: Ni/Al-Al_2O_3, Ni/Mg-MgO, Ni/Fe-Fe_2O_3, Zn/Ca-CaO, Cr/Al-Al_2O_3, Sr-CaO, Li-MgO, Zn-MgO, Ni-Cr, Co-Ni, Zn-CaO and Rb-K_2O Plots for Chalvad (o), Gandhra(•), Ambapani (▲) and Ranjitpura (▵) phosphorites.

The Ni/Al, Ni/Mg and Ni/Fe are found to be variable in these phosphorites (Tables XLIV to XLVII). When Ni/Al, Ni/Mg and Ni/Fe ratios examined in more details by plotting against Al_2O_3, MgO and Fe_2O_3 percentage (Fig. 13-A, B and C) they show negative relationship which suggests the replacement of Al, Mg and Fe by Ni. Nickel does not show any significant relationship with P_2O_5 but it shows good positive relationship with Cr and Co (Table XXXV and XXXVII). Many workers like Van Ingen (1915), Phillips (1917, 1922), Noddack and Noddack (1939) Bowen, V.T. and Sultan, D. (1951), Krauskopf, (1955), Le Riche, H.E. (1959), Nicholls and Loring (1962) Tourtelot, H.A. (1964), Gulbrandsen, (1966), Cook, (1972), Verma (1978), Raha (1978), Rao (1984), are of the opinion that Cr, Ni, Cu and Zn can be accummulated in sediment by the metabolic activities of organic matter.

Cobalt

Cobalt is a siderophile element and member of iron family (Goldschimidt, 1929) or ferrides (Landergren, S. 1943). Geochemically cobalt is closely related to nickel. The ionic radius of Co^{2+}(0.72 A°) is more or less identical to those of Ni^{2+}(0.69 A°) and Fe(0.74 A°). There is possibly a preponderance of cobalt over nickel in soluble products of weathering. The Ni^{2+} ion seems to be more stable in solution then that of Co^{2+} ion.

The concentration of cobalt in Chalvad, Gandhra, Ambapani and Ranjitpura phosphorites have an average value 56.22 ppm, 54.93 ppm, 52.11 ppm and 48.89 ppm (Fig. 11) respectively which is at higher side than the values reported by Gulbrandsen (1966),

Krauskopf (1955) but in the range of values reported by Prevot and Lucas (1979). The analytical results show weakly negative relationship with P_2O_5 (Table XXXV to XXXVII). However, Co shows close coherence with Ni, Fe_2O_3 (Tables XXXV to XXXVII). The positive correlation of Co with Cr, Ni, CO_2, Pb and Li (Tables XXXV to XXXVIII) suggest their adsorption by organic matter.

Lead

Lead occurs in the upper lithosphere both as chalcophile and as a lithophile element. In phosphate and silicate minerals it occurs mainly as Pb^{2+}. Lead (Pb^{2+}) appears intermediate in ionic size between Ca^{2+} and K^+ and thus it is expected to occur in the carbonate, K-feldspars and micas substituting potassium. The ionic radius of Pb^{2+}(1.20 A°) makes it possible to replace Sr^{2+} bond but Sr^{2+} is much larger and enter the K^+ position as readily as Ca^{2+} lattice sites (Heir, K.S. and Taylor, S.R. 1959). The Pb^{2+} ion shields PO_4^{3-} ion more effectively than Ca^{2+} ions in apatite where calcium occurs in nine fold co-ordination with oxygen thus act as a host for Pb.

Limestones and dolomites are generally low in lead. In these rocks its concentration is highly variable as evidenced 5 to 10 ppm by Rankama, K. and Sahama, T.G. (1950) and Krauskopf (1955), 16 ppm by Ostrom, M.E. (1957) and 7.2 ppm by Graf (1960).

The concentration of Pb varies from 18 to 69 ppm in Chalvad, 13 to 60 ppm in Gandhra, 13 to 50 ppm in Ambapani and traces to 41 ppm in Ranjitpura phosphorites. The concentration of lead in the adjacent dolomitic limestone, quartzites and phyllites vary from 11 to 17 ppm, traces to 10 ppm and 10 to 18 ppm respectively

which is very low when compared with the phosphorites of the area. Concentration of Pb appear to be higher in stromatolitic form species particularly *Conophyton-Colonnella* assemblage. The concentration of Pb in the studied phosphorites is in the range of the values as reported by Tooms et al., (1969). The positive relationship of Pb with P_2O_5 from Chalvad (r=0.37), Gandhra (r=0.76) and Ranjitpura areas (r=0.41) suggests that under favourable physico-chemical condition, Pb was rather separated from its original host mineral during weathering and transported in the form of soluble stable compound in association with carbonate minerals. It, therefore, probable that lead in the phosphate rocks is mainly influenced by the presence of stromatolites forming algae.

Zinc

Zinc is predominantly a chalcophile element. Clarke, F.W. and Washington, H.S. (1924) reported 40 ppm Zn in upper lithosphere. Zn is very mobile element and lies on the border between the soluble cations and the elements of hydrolyzates. Zn^{2+} shows geochemical relationship with Fe^{2+}, Mg^{2+}, Mn^{2+} and Ca^{2+}. It has been suggested that Zn^{2+}(0.74 A°) should able to replace Mg^{2+}(0.66 A°), Mn^{2+}(0.80 A°) and Ca^{2+}(0.99 A°) in calcite, but not to as great extent as Mn^{2+} (Berry, I.G. and Mason, B. 1959).

The concentration of Zn in calcareous rocks is reported as 50 ppm (Rankama and Sahama, 1950), 4 to 20 ppm (Krauskopf,1955), 35 ppm (Runnels and Schleicher, 1956), 45 ppm (Ostrom, 1957) and

16 ± 3 ppm (Graf,1960). The concentration of Zn in the study area varies from 33 to 81 ppm in Chalvad, 31 to 89 ppm in Gandhra, 32 to 88 ppm in Ambapani and 32 to 110 ppm in Ranjitpura with an average value of 64.78 ppm, 46.36ppm, 61.89 ppm and 67.94 ppm respectively (Fig. 11). Zn exhibits positive relationship with P_2O_5 (Fig. 12-F) with the value between 0.45 to 0.64 (Tables XXXV to XXXVIII). The positive relationship may be possibly due to the presence of algal stromatolites while its concentration in associated rocks i.e. dolomitic limestone, quartzites and phyllites ranges from 26 to 33 ppm, 16 to 21 ppm and 31 to 52 ppm respectively. The concentration of Zn in the studied phosphorites is lower when compared with the values given by Gulbrandsen (1966) and Prevot and Lucas (1979). It seems possible that the apparent defficiency of Zn in the stromatolitic phosphorites is more a function of weathering and leaching. The negative correlation coefficient value of Zn with MgO (Tables XXXV and XXXVII) in these phosphorites indicate the possibilities of the replacement of Mg^{2+} by Zn^{2+} possibly in calcium phosphate lattice. Zn/Ca ratios plotted against CaO percent (Fig. 13-D) does not show any significant relationship. The variability of Zn/Pb ratios (Tables XLIV to XLVII) and sympathatic relationship of Zn with Pb (Tables XXXVI and XXXVIII) indicate close coherence of Pb and Zn in these phosphorites.

Chromium

Chromium in phosphate and silicate rocks preferably occurs in pentavalent state and rarely in trivalent or hexavalent state. In silicate minerals it occurs as a cation outside the complex

silicon and oxygen framework. Because of the identical chemical properties, i.e. ionic size and ionic charge it can readily substitute Fe^{3+}(0.67 A°) and Al^{3+}(0.58 A°) didochically in silicate rocks. Cr usually behaves as a highly lithophile element. During disintegration and weathering of rocks, Cr^{3+} has little mobility and its behaviour is similar to that of Fe^{3+}. Cr, Pb, Se, Y and all lanthanoids though relatively depeleted in sea water, are enriched in phosphorites (Tooms, et al., 1969) and enriched in soil also (Reedman, J.H. 1984).

The concentration of Cr in carbonate rock as reported by Rankama and Sahama (1950) is 2 ppm; Krauskopf (1955) 5 ppm; Runnels and Schleicher (1956), 13 ppm; Ostrom (1957), 11 ppm; Graf (1960), 13 ppm and Turekian and Wedepohl (1961), 11 ppm. The concetration of chromium in these phosphorites has been reported to be very high (Tables XXXIX to XLII) which vary from 72 to 143 ppm in Chalvad, 12 to 155 ppm in Gandhra, 25 to 134 ppm in Ambapani and traces to 113 ppm in Ranjitpura area. The concentration of Cr in dolomitic limestone vary from 16 to 27 ppm whereas quartzites and phyllites are having high Cr content (Table XLIII) perhaps due to the presence of high Fe^{3+} content and micas.

Cr exhibits negative correlation with P_2O_5 (Fig. 12-D) which indicate that apatites do not have any coherence with Ni. But the positive correlation of Cr with Fe_2O_3, CO_2, Ni and Co (Tables XXXV to XXXVIII) might be due to the presence of organic matter (Vinogradov, A.P. 1953, Krauskopf 1955, Gulbrandsen, 1966 and

Rao, 1984).

In Chalvad, Gandhra and Ranjitpura phosphorites Cr shows close coherence with the element related to silicate mineral as it is evident by its positive correlation coefficient with SiO_2, Fe_2O_3 and K_2O. Hirst, D.M. (1962) and Nicholls and Loring (1962) determined the relationship between Cr and Al content. The variable Cr/Al ratios plotted against Al_2O_3 percent (Fig. 13-E) shows an inverse relationship suggesting substitution of Cr^{3+} for Al^{3+}. According to Frahlich, F. (1960) the bulk of Cr present in sediment is found to be associated with micas and clay minerals, mainly illite. Prevot and Lucas (1980) proposed that Cr is primarily carried away by the apatites and is fixed in clays.

Strontium

Strontium is a lithophile element and occurs as oxysalts in residual sediments. The crystallo-chemical parameters of Sr^{2+}(r=1.18, e=1.0, i=1.69) are closely similar to those of Ca^{2+} (r=0.99, e=1.0, i=2.02) and Pb^{2+} (r=1.18, e=1.6, i=1.67). The virtually identical ionic radii of Pb and Sr suggest the replacement of the former by the latter in some lead minerals. Sr is usually found in large amount in calcium-rich minerals and to lesser extent in potassium-rich minerals. This phenomena is explained by Goldschimidt's `admittance' theory, which says that Sr^{2+} is admitted into the smaller calcium lattices but is entrapped in the potassium lattices which has a larger radius.

In carbonates, the strontium content varies widely as reported by Rankama and Sahama (1952), 425-675 ppm; Krauskopf (1955), 400-800 ppm; Runnels and Schleicher (1956), 470 ppm;

Ostrom (1957), 490 ppm and Graf (1960), 420 ppm.

It is well known that Sr is strongly concentrated in phosphorites as determined by Krauskopf (1955), Gulbrandsen (1966) and Prevot and Lucas (1979, 80). From the available data of the world phosphorites it appears that Sr generally related positively with the P_2O_5, rarely with calcite and never with Al_2O_3 (Prevot and Lucas, 1980). Thus it can be logically concluded that strontium shows its preferential association with the apatite. However, Sr and P_2O_5 are not strictly proportional. It is also known that phosphorus concentrates in soft parts of micro-organisms and may hold upto one percent strontium in tests and shells (Kulp, J.L. et al., 1952). During weathering strontium is quickly lost to the apatite lattices (Lucas et al., 1980) and even to the phosphorite.

The present study reveals that Sr content in study area is on lower side (Tables XXXIX to XLII) when compared with values given by Gulbrandsen (1966) and Lucas et al., (1980). The average concentration of Sr is 138 ppm in Chalvad, 183 ppm in Gandhra, 127 ppm in Ambapani and 208 ppm in Ranjitpura deposits (Fig. 11). Sr is positively related with P_2O_5 (Fig. 12-H) and CaO (Fig. 13-F) which indicates that Sr incorporated in carbonate apatite structure at the time of its formation and remain fixed during any post depositional alteration. The low Sr/Ca values (Tables XLIV to XLVII) in these phosphorites relative to any admixed $CaCO_3$ implies that Sr content was also derived from another source in addition to those present in calcium carbonate mineral.

Rubidium

Rubidium is a lithophile element and shows close coherence with potassium. Rb apparently penetrates into the lattices of clay minerals where it replaces potassium (Horstman, E.L., 1959). Of all the alkali matels Rb possesses the highest tendency of interstitial capture and more readily adsorbed in clays than potassium (Goldschimidt, 1937). The bulk of Rb, that is released during weathering of igneous and metamorphic rocks enter partially into the crystal lattices of clays as a result of adsorption.

According to Wedepohl (1970), the abundance of Rb in dolomitic limestone varies from 6-370 ppm and in silty limestone 6-167 ppm. In study area, the Rb content varies from traces to 23 ppm in Chalvad, traces to 17 ppm in Gandhra, traces to 30 ppm in Ambapani and Ranjitpura phosphorites while its content varies from traces to 9 ppm in associated dolomitic limestone, 9 to 17 ppm in quartzites and 78 to 96 ppm in phyllites of study area.

Rb does not show any significant relationship with P_2O_5 (Fig. 12-I) which indicates noncoherence of Rb with the elements related to apatite. The strong positive correlation coefficient of Rb with K (r=0.55 to 0.97) and relatively constant K/Rb ratios (Table XLIV) suggest their close coherence with potassium. Rb also have positive correlation coefficient with silica, alumina and Rb/Al ratios clearly indicate that Rb is possibly due to the presence of clay minerals in these stromatolitic phosphorite.

Lithium

Lithium is an alkali metal and strongly lithophile in its geochemical character. In many respects lithium follows magnesium since magnesium acts as a protective element for lithium. Strock, L.W. (1936) suggested that the replacement of Li by Mg is possible only when electrical balance of the structure is maintained by the introduction of a trivalent six co-ordinated cation. Li^{+} (r=0.68, e=0.95) form more ionic bond with oxygen than either Mg^{2+}(r=0.66, e=1.20) or Fe^{2+} (r=0.74, e=1.70).

The concentration of lithium in various rocks were reported by many earlier workers. Rankama and Sahama (1950) reported 46 ppm of Li in shale, whereas Strock (1936) reported 26 g/ton of Li in limestone. Solodov, N.A. (1961) quoted upto 0.15% of Li in apatite.

The concentration of Li in studied phosphorites vary from 5 ppm to nil in Chalvad, Gandhra and Ambapani areas whereas in Ranjitpura phosphorites show traces to 7 ppm Li. The extremely low content of Li and scatter relationship with P_2O_5 (Fig. 12-G) indicate noncoherence of Li with P_2O_5. But in Ranjitpura phosphorites Li show positive correlation coefficient with P_2O_5 (Table XXXVIII). However, the negative relationship of Li with MgO (Tables XXXVI to XXXVIII) indicate replacement of Mg^{2+} by Li^{+}. The positive correlation coefficient of Li with Ni, Co, Cr (Table XXXV), Co, Pb (Table XXXVI), Cu, Co, Pb and Zn (Table XXXVII) indicate that Li was possibly influenced by the algal stromatolites.

Cadmium

Cadmium is predominantly a chalcophile element in its geochemical character and behaves very much like that of Zn. The close similarities of the ionic radii of Cd^{2+}(0.97A°) and Ca^{2+}(0.99A°) suggest that these elements are closely associated with each other in nature (Sandell, E.B. and Goldich, S.S. 1943 and Rankama and Sahama, 1950).

The geochemistry of Cd during sedimentation processes has not yet been studied in details by any previous worker. Hence no reliable data is available for the distribution of Cd in sedimentary formations. Cd was determined in marine phosphorites by Rankama and Sahama (1950), Haberland, H. (1947) Malinovskii, F.M. (1955) and Kholodov, V.N. (1959). A range from 0.000015 to 0.003 percent Cd in apatite was quoted by Noddack, I. (1935).

The concentration of Cd in these phosphorites varies from traces to 10 ppm in Chalvad and Ambapani, 5 to 10 ppm in Gandhra and Ranjitpura area. The nearly constant concentration of Cd shows a weak positive relationship with P_2O_5 and CaO.

DISCUSSION

Geochemical methods have received increasing emphasis in recent years as a means of reconstructing the ancient environment. An attempt has been made here to find out the environmental conditions under which these phosphorites are formed, on the basis of the geochemical association, behaviour and distribution pattern of various trace elements determined.

From the proceeding discussion of the individual element, it appears that considerable amount of trace element entered in the basin of deposition, adsorbed and structurally entered the lattices of various minerals. The variable concentration of trace elements in these phosphorites have been influenced by various physico-chemical processes involved during weathering and leaching of the pre-existing rocks and subsequently they were added to the sediments in traces. The adsorption of some trace elements was mainly influenced by the principal absorbants like phosphate minerals, organic matter, clay, iron and silicate minerals.

Sr, Cr, Pb and Zn are the elements which are susceptible to adsorption by phosphate minerals. The elements which were possibly adsorbed by the organic matter include Ni, Co, Cr, Pb, Zn and Cd. Elements adsorbed by clay minerals include Rb and possibly Li. Trace elements dispersion in the phosphorites associated with fossil algae suggest that fixation of Cu, Ni, Co, Cr, Pb, Zn and Cd was geochemically controlled by biogenic activity of the algal matter under shallow marine environmental conditions. The close association of trace elements, viz. Ni, Co, Pb and Zn with organic metabolism was suggested by many of the workers namely Van Ingen (1915), Van Ingen and Phillips (1915), Phillips (1917, 1922), Noddack and Noddack (1939), Bowen and Sultan (1951), Krauskopf (1955), Gulbrandsen, (1966), Le Riche (1959), Nicholls and Loring, S.R. (1962), Tourtelot (1964), Raha (1978), Verma (1978), Rao (1984), Ali, (1990), Khan, K.F. (1991).

Chapter VIII

ORIGIN OF PHOSPHORITE

Introduction

The complexity of the processes involved in the formation of marine phosphorite deposits has been the subject of study by a large number of workers through an early period in which basic disagreements existed between scientists concerning the mode of deposition. However, from a general review of the work on the important phosphorite deposits of the world it may be said that the formation of phosphorites was essentiallly controlled by certain inter related geological, biogenic and chemical factors. Gulbrandsen (1969) pointed out the significance of organic activity for the formation of phosphorite. Buckland, W. (1829) suggested the mode of phosphorites deposition through coprolites, decomposition of seaweeds and animals by Seeley, H. (1866), precipitation from solutions secreted by animal agency (Fisher 1873), animal remains through mass mortalities (Cornet, M.F.L. 1886), redeposition of phosphate dissolved from bones and phosphatic matter from dead animals (Penrose, R.A.F. 1888), planktons (Murray, J. and Renard, A.F. 1891), fish remains (Blackwelder, 1915, 1916) and deposition in swamps in association with peat (Penrose 1888). Blackwelder, E. (1916) described the geochemical cycle of phosphorus from its source in igneous rocks, through its path in biologic cycle, its storage in the ocean, its sedimentation and its reincorporation in the earth's crust. Grabau, A.W. (1919) pointed out that phosphate beds occur at

minor and major unconformities. Pettijohn, F.J. (1926) interpreted the zones of phosphatic limestone which are rich in phosphatic nodules as a residuum on corrosion surfaces due to submarine erosion. Kazakov, A.V. (1937) prosposed a new hypothesis of upwelling water current, which was advanced by earlier workers and added more of his own ideas to formulate a comprehensive model that dealt with the origin and localization of phosphorous, its mode of deposition, palaegeography of depositional basins, geological environment, geometry of beds and the petromineralogy of the phosphorites.

Mansfield, G.R. (1940) made an attempt to correlate the Period of phosphate deposition within the geologic record of the periods of wide spread volcanisms. Mansfield stated that unusual addition of fluorine to the ocean from hydro-fluoric vapour, emanated from volcanoes, might have lowered the solubility of apatite resulting in its chemical precipitation. Gimmel'farb, A.P. (1957) and Ronov A.B and Korzhina (1960) pointed out a broad cyclic increase and decrease in phosphate deposition through ages and suggested that the deposition was more pronounced in Silurian, Permian, Cretaceous and Tertiary periods.

McKelvey, V.E. and others (1953) modified Kazakov hypothesis by explaining the Permian phosphorites of Rocky Mountains. Kazakov (1937) pointed out that phosphorus content in the ocean water increases with depth from a minimum in the zone of photosynthesis to a maximum at about 500 meters. Phosphate is precipitated on shelving, shallow ocean bottoms where deep, cold and phosphorus-rich waters ascend. Physico-chemical changes in

ascending water include increasing temperature and decreasing partial pressure of CO_2 which cause phosphate deposition. Kazakov reasoned from the standpoint of solution chemistry and hydrographic data that below 200 meters the cold water contained enough dissolved CO_2 to be undersaturated with respect to apatite. Above 50 meters, in the zone of photosynthesis, the available phosphorus is assimilated by phytoplankton and no apatite is deposited. Thus the geographic environment of phosphorite deposition seems to be continental shelf at a depth of 50-200 metres in the areas of ascending deep ocean water. The phosphorite facies probably deposited with synchronous shallow water sediments on the shoreward side and deep water sediments on the basinward side. Two phosphorite facies viz.,the shallow-water plateform facies, which is distinguished by nodular, pebbly phosphorites, low to moderate P_2O_5 content, and associated with the glauconitic and arenaceous materials, the deep water geosynclinal facies which is characterised by thin bedded phosphorite with high P_2O_5 content, occurs associated with limestone and shales. The quality of phosphorites depend upon the composition of enclosing rocks and on the relative sedimentation rates of terrigenous material and phosphates. Kazakov discarded the biogenic hypothesis with the chemogenic elements of his hypothesis. He also discarded the hypothesis requiring volcanic activity for the formation of phosphorites. Bushinski, G.I. (1966a,b), a colleague of Kazakov opposed strongly the idea of Kazakov and published in criticism along with an historical summary on the origin of phosphorites. At

present, many, if not most phosphorite petrologists accept the Kazakov hypothesis with some modifications.

Gulbrandsen (1969) pointed out that the optimum conditions for the formation of large amount of apatite seems to be the coincidence of a special steady supply of phosphate, originally derived from organic matter and decreased capacity of seawater for phosphate. He suggested that these conditions were best fit in shallow parts of seas on continents where large amount of organic matter accumulated in oxygenated waters of higher than normal temperature, pH and salinity.

Martens and Harriss (1970) pointed out that the Mg/Ca ratio in seawater sufficiently high to inhibit the apatite precipitation from the ocean, a conclusion later supported and enlarged by Atlas, E.L. (1975). Stumm, W. (1972) also noted that the return of phosphorus to solution by oxidation of organic debris librates large amounts of CO_2, causing a lowering of pH. As suggested by Blackwelder (1916) and Bushinski (1966b), anaerobic bacterial action provides an alternative to oxidation for releasing the phosphorus to the solution from the organic matter. Blackwelder (1916) stated that anaerobic bacterial action yields ammonia, H_2S, phosphate, hydrocarbons and CO_2, depending on the supply of oxygen. In the early 1970s intensive marine geologic work confined that the process of anaerobic sulphate-reducing bacterial action on organic oozes produced interstitial water of high alkalinity and phosphate content and low magnesium content and that apatite pellets form chemically in this diagenetic environment. This diagenetic process produces

phosphatic pellets but not phosphorite, (Baturin, G.N. 1971). However Baturin (1971) proposed that slightly phosphatic muds could be reworked at times of lower sea level, thereby washing away the mud and concentrating the apatite pellets. The Baturin's hypothesis of "Upwelling currents-diagenetic precipitation-low sea level reworking" accepted by many geoscientist such as Cook, P.J. (1976), Kolodny, Y. (1980). Burnett, W.C. (1977) initially acceptedthe hypothesis but later expressed reservations regarding the universality of application of the hypothesis (Burnett 1980) and questioned the hypothesis as a mechanism for producing the marine phosphorite deposits (Sheldon, R.P. 1980) and following hypothesis developed by Fisher, A.G. and Arthur, M.J. (1977), presented an alternative non-uniformitarianism hypothesis of episodic phosphogenesis.

Pevear, D.R. (1966) proposed river as a source of phosphorus and suggested estuarine depositional environment. Rooney and Kerr (1967) proposed that a volcanic tuff fall which killed large number of organisms whose decay contributed the source for the phosphorus. Gibson, T.G. (1967) presented evidence of cold current to the Gulf stream coming down along the eastern United States Coast from the north at the time of deposition of the phosphorite. Cathcart, J.B. (1968) accepted Gibson's hypothesis and expanded it. Freas, D.H. (1968) postulated local upwelling currents along the coast in conjunction with the ancient northward flowing Gulf current. Riggs, S.R. (1979) proposed that hydrothermal solutions rich in phosphorus "exhaust onto the sea floor" and "supercharge the

marine environment" and then "oceanic current systems" and associated upwellings mix and move the supercharged waters up into the shallow water environments.

Sheldon (1981), pointed out that marine phosphogeneis consists of oceanographic, sedimentational, diagenetic and erosional processes. These basic processes include - i) Supply of phosphorus to the ocean ii) Storage of dissolved phosphorus in the deeper water of the ocean iii) circulation of deep water to shallow levels iv) concentration of phosphorus on the sea bottom v) solubility changes of ocean derived water with respect to apatite vi) precipitation of apatite and vii) concentration of apatite.

According to Slansky, M. (1986) phosphate deposits are mainly supplied with phosphorus from deep oceanic reserves by means of upwelling currents. Phosphate minerals precipitate from the interstitial water near the water sediment interface and the margins, particularly the upper boundary of O_2 minimum layer. Oxidizing encourages stability of the humic compound formed from planktonic organic metter,the humic acids seems to play a direct role in the phosphate precipitation.

Baturin (1989), suggested that sedimentation ,diagenesis and subsequent transformation control the compositions of marine phosphorites. The role of the first two factors can be judged from the composition of the phosphorites and the enclosing sediments.

Various views mentioned above have been expressed on the source of phosphorus, stratigraphic relations, the sedimentation

processes, and the timing of events. But one can conclude that there are three main schools of thought regarding the genesis of phosphorites

i) Organic origin based on their association with true coprolites, and skeletal materials (Buckland 1829; Seeley 1866; Fisher 1873; Cornet 1886; Penrose 1888; Murray, and Renard, 1891; Blackwelder 1915,1916, etc.).

ii) Replacement of previously calcareous bioclasts or lithoclasts (Cayeux, L. 1950, Lucas, et al., 1977, Ames 1959, etc.).

iii) Inorganic origin of phosphorites (Kazakov, 1937, McKelvey, 1967, McKelvey and others, 1953, Cheney, T.M. 1955; Sheldon, 1964, 1981, etc.).

The recent findings of sedimentary phosphorite deposits belonging to the Champaner Group of the Aravalli Super Group has a strong similarity with the phosphorite deposits of Aravalli Super Group of Rajasthan which are marine sedimentary phosphorite (Muktinath, et al., 1972). In the light of the foregoing views of phosphogenesis an attempt has been made to discuss the geologic, biogenic, and chemical controls of the formation of phosphorite in the area of interest.

Geological Controls

The phosphorite bearing horizon of the study area appears to be related to the facies changes from argillaceous phyllite into dolomitic limestone as the phosphorite bodies are present along the lower part of dolomitic limestone overlying the phyllite. The

repeatative sequence of conglomerate indicates that the basinal conditions were fluctuating and the presence of benthonic algae clearly indicates a shallow to very shallow depositional condition. A sharp decrease in thickness and even wedging out of the phosphorite bed in the direction of the strike indicates lacunae in sedimentation.

The source of phosphorus seems to be adjacent granite and other rocks from where phosphorus along with silica and lime were derived as a result of weathering and chemical decay. Furthermore the complete absence of phosphate in associated carbonate lithofacies and its restricted occurrence within the stromatolites alone indicates that the pure physico-chemical system could not operate the phosphate deposition in the study area. The complex biochemical system engineered by the micro-organism involved in the growth of stromatolite could play an important role in the deposition of phosphorites (Chauhan, and Sisodia, 1981). It appears that due to marine upwelling the phosphatic material accumulated in marine environment got concentrated in a more or less restricted basin of deposition. Certain favourable physico-chemical conditions supported the growth of colonies of algae in this part of the ancient sea to maintain their metabolic activities. The distribution of phosphorite as discontinuous lenses is appear to be largely controlled by basinal topography. The topographic highs were perhaps the selected places of high phosphate accumulation while in the relatively deeper parts of the basin low grade phosphorite with the dolomite matrix was formed. It is,

therefore proposed that volcanism during sedimentation of Khandia Formation may have contributed to enrich the bottom sea water in phosphorus and localised upwelling near basement highs brought in phosphorus rich nutrient water at the site of deposition.

From the preceeding discussion it appear that the formation of phosphorites have been largely influenced by the following factors operating exclusive of each other or in combination. i) excess charge of phosphate in certain zones of the basin, ii) preferential development of stromatolites iii) facies variation and iv) penecontemporaneous and post depositional deformation.

The petrographic study indicate that the phosphorite was formed due to progressive replacement of calcite by collophane. Microscopic examination of these stromatolites show that they are composed of alternate laminae of cryptocrystalline to microcrystalline collophane and fine to medium grained calcite and dolomite with or without quartz.

Biogenic Controls

The phosphorite deposits of Panchmahals occur associated with the carbonate rocks, confined to the Khandia Foramtion at Chalvad, Gandhra, Ambapani and Ranjitpura. These phosphorite deposits occur in close association of algal stromatolites. It is well known that algae help in the precipitation of phosphorite from seawater. But the views on the process of deposition, precipitation and fixation of phosphorite by algae in sea water differ considerably. Charles, G. (1953) postulated that the benthonic algae, which grow in shallow sea floor (photic zone),

accumulate phosphorus from phosphorite. In addtion to the blue green algae the stromatolites also contain structurally preserved fossils of bacteria (Schopf, J.W. 1968; Cloud and Semikhatov, 1969) which directly or indirectly aided the localisation of phosphate (Emigh, G.T. 1969). Banerjee (1971) has suggested that the algal stromatolites might have played an important role intrapping and precipitating the dissolved inorganic phosphorus from the sea water.

The phosphorites of the study area are found to be closely associated with the algal stromatolites. The form species identified includes *Collenia columnaris, Colloenia baicalica, Conophyton, Colonnella, Kussiella kusiensis* and *Tungussia Semikhatov*. The occurrence of benthonic phophatic algal stromatolites in these phosphorite deposits of Panchmahals appear to be largely restricted to the zone of photosynthesis in subtidal to intertidal environment. The benthonic algae flourishing in phosphate bearing intertidal to subtidal water was responsible for building the carbonate structure (Stromatolites) on one hand and on the other, changing the marine environment through their biotic activities (photosynthesis and metabolism). It is reasonable to believe that the algae initiated accumulation and precipitation of phosphate by almost contemporaneous and progressive replacement of the developing carbonate structure.

In the study area the restricted occurrence of phosphate mainly within the stromatolite framework suggests that some specific community of micro-organisms involved in the growth of stromatolites must have controlled the process of phosphorite

formation during that time. The actual process of the formation of stromatolitic phosphorite is much more complicated. Recent studies, on the formation of phosphorite indicate direct precipitation of phosphate in the body of the accreting stromatolites (Banerjee, 1971b; Banerjee et al., 1980; Southgate, P.N. 1980) and progressive replacement of initially developed calcium carbonate structures under the persitent influence of microbial community involved in their growth (Chauhan and Sisodia 1981).

Collenia columnaris which is charaterissed by highly tight packing with little or no interclomunar spaces and stout growth, did not favour the precipitation of phosphates and appears non-phosphatic whereas *Collenia baicalica* which have large intercolumnar spaces, branching stem and sparsely arranged convex lamina, are highly phosphatic. They possibly served as ideal hosts for the accumulation of phosphatic sediments. These stromatolites also occur in laminated and pelletal forms. The laminated and pelletal columns of these stromatolites are phosphatic whereas the ground mass, which is mostly dolomitic is either non-phosphatic or feebly phosphatic, It, therefore, appears that the stromatolites might be responsible for absorbing and reprecipitating the dissolved inorganic phosphatic material from the sea water under shallow marine conditions. The presence of organic matter and stromatolites conclusively suggest that the formation of Panchmahals phosphorites was partly controlled by biogenic activities in shallow marine water under slightly

reducing to fairly oxidizing conditions.

Chemical Control

The chemical factors which appear to control the formation of phosphorites are reviewed and discussed. The following chemical factors appears to have affected the formation of phosphorites of the study area :

1. Effect of pH
2. Effect of Eh
3. Effect of temperature and pressure
4. Effect of geochemical behaviour of major and trace elements

1. Effect of pH

The deposition of phosphorite as well as the carbonates is supposed to be mainly controlled by pH condition. According to Kazakov (1937), the precipitation of phosphorite takes place at pH values of about 7.1 and that of calcium carbonate at pH values 7.1 and 7.8. Simultaneous precipitation of calcium phosphate and clacium carbonate may also take place when pH is about 7.8, but the ratio of calcium carbonate would be much higher in this case due to its high absolute solubility (Krumbein, W.C. and Garrels, R.M. 1952). Campbell, C.V. (1962) postulate that phosphorite precipitates predominantly in the pH range between 7.1 and 7.8 and calcium carbonate, when pH is higher than 7.8. McKelvey, et al., (1953), while discussing the genesis of phosphorites of the Phosphoria Formation of North America remarked that when cold phosphate-rich water upwelled into the large shelving embayment from the ocean, phosphorite was precipitated in the ascending waters as their pH increased along with the increase in

temperature and decrease in partial pressure of CO_2.

The carbonates were deposited from these waters when they reached more shallow depth at somewhat higher pH. Thus, it is reasonable to derive that the chemical environment of phophate precipitation is principally dependent on hydrogen ion concentration (H^+) as given in the following reactions :

$$H_3PO_4 = H_2PO_4^- + H^+,$$
$$H_2PO_4^- = HPO_4^{2-} + H^+,$$
$$HPO_4^{2-} = PO_4^{3-} + H^+,$$

It therefore, appears that PO_4^{3-} concentration is dependent on the pH of the system which is primarily controlled by the reactions of CO_2 and water to give carbonic acid, so that the increase of dissolve CO_2 tends to lower the pH at any given alkalinity (see Sheldon, 1981). PO_4^{3-} forms a number of complex ions, of which perhaps the most important to seawater phosphorus reactions is $MgHPO_4$ ion (Atlas 1975). Any such complex ion formation reduces the concentration of PO_4^{-3} ion.

In case of copercipitation of calcite and apatite, the calcite-apatite ratio will be higher, since Ca_3^+, PO_4^{3-} and CO_3^{2-} have a single valence state and as such change in Eh cannot produce separation into carbonate rich or phosphate rich layers, and hence the individual enrichment may take place witnin a narrow pH range. $Ca_3(PO_4)_2$ is less soluble in comparison to CO_3^{2-} (since the solubility product of $CaCo_3$ is 4×10^{-9} as against 1.3×10^{-30} for $Ca_3(PO_4)_2$). Hence, $Ca_3(PO_4)_2$ precipitated first in the pH range 7.1 to 7.8 while CO_3^{2-} remained in solution so

long as the pH is buffered in this range. With the rise of pH to 8 or above precipitation of calcium carbonate is started.

In the study area, the higher calcium carbonate/calcium phosphate ratio and preferential accumulation of phosphate in the algal stromatolites indicates that pH remained 7.1 and 7.8. Noctidiurnal changes in the life activities of algae would be possibly more effective to create favourable conditions for the precipitation of phosphate. During day time photosynthetic activities of alga possibily increased the pH by consuming CO_2, whereas during night time algal metabolism should lower pH by releasing CO_2. These changes are likely to maintain pH of water surrounding the algal growth below 7.8 and favour the precipitation of phosphate and carbonate at pH above than 7.8. The absence of phosphorites in the thick carbonate lithofacies associated with the phosphorite deposits and even in intercolumnal material of stromatolites indicates the pH value more than 7.8 where carbonates were deposited.

2. Effect of Eh

The primary precipitation or replacement of calcium phosphate need not be influenced by Eh. The state of oxygenation in a given environment indirectly plays a role of controlling the rate, extent and nature of release of phosphate from the other basins in the ocean (Bortleson, G.C. and Fredlee, G. 1974). Phosphorus has a strong tendency to be associated with iron in many aquatic environment. Subramanian, V. (1976) has showed that iron and phosphorus are cogenetic in freshwater as well as in esturin environment. In a highly oxidizing environment, Fe^{3+}

removes P from water by the formation of sorbed complex $Fe(OH)_3$, thereby making available only a small amount of PO_4^{3-} for Ca^{2+} to form apatite in marine environment. The values of Fe_2O_3/FeO (Tables XI to XIV) indicate slightly reducing to fairly oxidising shallow water conditions for the precipitation of phosphorites in the area of interest.

3. Effect of pressure and temperature

Since temperature affects the solubility of many minerals and gases, it has therefore, an important effect on chemical precipitation. At lower temperature the solubility of CO_2 is greatly enhanced. Hence the solution of calcium carbonate is promoted in cold water and conversely precipitation of the same material is brought about by a rise in temperature.

According to Berner, R.A. (1971) the temperature ranges from 20°C at the surface to 2°C at the bottom of the oceans with the pressure change from 1 atmosphere to 500 atmosphere. Pressure and temperature have opposing effects on the phosphate solubility but the constant values for dissolved phosphate at depths below 1000 meters indicate that the pressure effect on the phosphate equilibria is negligible. The involvement of CO_2 in the carbonate equilibria was responsible for the quantitative changes in carbonates associated with phosphate deposits. Like carbonates, phosphates are also dissolved at greater depths and probably reprecipitated at shallow depth since a decrease of temperature and an increase of pressure increases the solubility product or make apatite more soluble (Sheldon, 1981).

Kramer, J.R. (1964) calculated solubility products for carbonate fluorapatite, which show small decrease in solubility of phosphate with increase in temperature over a representative of natural conditions. The indirect effect of temperature is possibly due to the antipathetic relationship between temperature and CO_2 solubility. As pH is invsersely related to CO_2 solubility, pH and temperature are naturally related. Hence an increase in temperature is likely to cause an increase of pH and a decrease of solubility of phosphorite and vice-versa.

4. Effect of geochemical behaviour of significant major and trace elements

Apatite represent a group of minerals containing Ca^{2+} and PO_4^{3-} as essential contituents with associated trace elements among which Mg, Mn, Sr, K, Na, Ba, Cr, Fe, Al, VO_4^{3-}, SO_4^{4-}, CO_3^{2-}, F^{-1}, Cl^{-1}, and OH^{-1} are important. It has been experimentally shown (Bachra, et al., 1965; Marten and Harris, 1970) that Mg^{2+} ions inhibit the precipitation of apatite probably because Mg^{2+} compete with Ca^{2+} in the apatite structure. Marten and Harriss (1970) deduced threshold values for the Ca/Mg ratio necessary for apatite to precipitate from solution. The magnesium ions seem to retard the reaction (salinity) when Ca/Mg values approach to 4.5 to 5.2. This ratio remains almost constant in normal sea water. Pore water is however, known to vary greatly from the sea water values. Thus it seems that diagenetic reaction occurring with anoxic sediment could raise the Ca/Mg ratio to the point (5.2) where phosphorite may precipitate. Nathan and Lucas (1976) conform this lower

limit of 5.2 for the Ca/Mg ratio for sea water with a pH value of 7.8 to 8.1.

The experimental work carried out by Morse (1979), Nathan and Lucas, (1976 and 1984) suggest a path way for the genesis of apatite and indicate conditions for its formation, which could prevail within the sediments in very shallow water during the very early diagenetic stage.

In the study areas, the high Ca/Mg ratio in few samples may be due to preferential entrace of Ca^{2+} ions in carbonate apatite, whereas low Ca/Mg ratio may be due to replacement of magnesian calcite by carbonate apatite. The anitipathetic relationship of MgO with CaO (Tables XXXV to XXXVIII) suggests that Mg^{2+} could be subsituted by Ca^{2+} in the apatite structure . The antipathetic relationship of CaO and P_2O_5 with MgO suggests replacement of dolomitic limestone by calcium phosphates. The antipathetic relationship of MgO with CaO and P_2O_5 also indicates that the surficial leaching had a leading role in the increase of P_2O_5 content, predominantly at the expense of MgO. It, therefore, seems possible that the replacement involving carbonates may be responsible for the increase of Ca/Mg ratio. The combination of these reations perhaps controlled the Mg^{2+} concentration in Mg-rich phases and the distribution of phosphorites in sediments.

In the study area, the CaO/P_2O_5 ratio is greater than 1.31. The higher values of CaO/P_2O_5 may be either due to the substitution of PO_4 by CO_3 in the apatite, or due to the presence of calcite or dolomite (Slansky, 1986). The sympathetic

relationship of H_2O^+ with CaO/P_2O_5 ratio suggests the possibility of substitution $PO_4 \rightleftharpoons (OH)_4$ as suggested by McConnell (1952). It has also been observed that samples having higher Ca/P + C values also have high H_2O^+ content and vice-verse, indicating the substitution of $(OH)_4$ by (PO_4).

Subramanian (1980), postulates that the chemical affinity between apatite and fluoride is so considerable that apatite is often used as filters to remove fluoride from drinking water. Thus fluoride in association with Ca^{2+} fixes phosphorus from sea water into the sediment. The source of fluoride may be submarine volcanism, spring water or even groundwater. Mansfield (1940) speculated that unconformities associated with phosphorite deposits may locally represent periods of active volcanism, causing the fixation of F and P into fluorapatite. The sympathetic relationship of F with P_2O_5 clearly indicate that with the increase of F the precipitation of calcium phosphate also increases. The partial replacement of F by oH is also fairly frequent in sedimentary apatite. In the study area it appears that CO_3^{2-} and OH are the principal substitutions for $(PO_4)^{3-}$ as proposed by Lehr, J.R. et al., (1967) in his experimental work. The experimental work carried out by Fisher and McConnel (1969) indicate a partial substitution of PO_4 by AlO_4, associated with the replacement of part of the Ca by Al. In the study area the negative relationship of SiO_2 and Al_2O_3 with P_2O_5 possibly indicate the substitution of P_2O_5 by Al and Si to minor extent.

An attempt has been made to represent the chemical reactions which are likely to occur in these sediments during diagenesis,

as follows:

1) $2\ CaCO_3 + Mg^{2+} \ ===\ CaMg(CO_3)_2 + Ca^{2+}$
Calcite Dolomite

2) $5\ Ca^{2+} + 3PO_4^{3-} + F^- \ ===\ Ca_5(PO_4)_3F$

3) $Ca_5(PO_4)_3F + 3HCO_3^{3-} \ ===\ Ca_5(PO_4.CO_3)_3(F.OH)+4H^+$ and/or

4) $5Ca^{2+}+3PO_4^{3-}+3HCO_3^{3-}+F+2H_2O \ ==\ Ca_5(PO_4.CO_3)_3(F.OH)+H_2O+4H^+$

5) $Al_2Si_2O_5(OH)_4+2HPO_4^{2-} \ ===\ 2AlPO_4.2H_2O+2SiO_2+H_2O$

6) $2AlPO_4.2H_2O+KOH \ ===\ KAl_2(PO_4)_2OH.2H_2O+2H_2O$

The above generalized chemical reactions show the complete stoichiometry of the reactants and products. Reaction (1) is related to the mechanism of dolomitization. Reactions (2,3 and 4) are mechanism proposed for the formation of phosphorite. Although there is little evidence to support the reactions (5) and (6) as shown by Nriagu, J.O. (1972) in shallow marine sediments, but the reactions (1,2,3 and 4) seem to be quite reasonable. The reaction (2) which involves precipitation of apatites, is applicable to its normal composition and the reactions (3) and (4) are related to carbonate apatite which is most common in the study area.

Model of Phosphorite Genesis

In the light of foregoing statements of facts and discussions, the most likely combination and sequence of events leading to the formation of phosphorites in the study areas are presented as follows:

The Precambrian phosphorites of Panchmahals are characteristically of sedimentary origin and were deposited in shallow marine conditions as evidenced by the presence of phosphorite association with dolomitic limestone and benthonic alga.

The source of the phosphate may be adjacent granite and other older rocks from which apatite bearing minerals contributed phosphates to the sea basin. Phosphorus was also extracted from the sea water by the organisms like phytoplankton and micro-organisms as an essential constituents of life. Such precipitation is controlled by the pH changes which in turn is related to the CO_2 concentration and upwelling of the sea water. The phosphorites are, therefore, attributable to shallow marine environment with subsequent marine upwelling bringing nutrients and phosphorus for fluorishing algal flora. It seems that lime, phosphorus and silica were brought to the depositional basin from the chemical weathering of granite and other older rocks by the transporting agencies and release the constituents in true solution or in colloidal state. Because of marine upwelling the phosphatic materials was concentrated in more or less restricted basin of deposition occupying arms of pre existing sea on the

embayment and shelf areas of the geosynclinal basin where a bluish green algal flora flourished.

The stromatolitic alga belonging to *Collenia, Conophyton, Collonella* and *Kussiella* groups were grown and developed colonies in this shallow sedimentary basin under suitable conditions of photosynthesis, upwelling, high pH(slightly above 7.5) and warm sunny climate under aerobic condition. It seems that the accumulation and absorption of phosphate minerals was dependent on their gross forms, size, structure and available intercolumnar spaces. Thus, these stromatolites appear phosphatic while the groundmass which is mostly calcareous and dolomitic are non-phosphatic or slightly phosphatic. It is, therefore, suggested that the stromatolites were responsible for absorbing and reprecipitating the dissolved inorganic phosphatic material from the sea water under favourable conditions.

Petrographic studies of these phosphorites reveal that these phosphorites were formed due to progressive replacement of initially developed algal carbonate structure by collophane. The replacement was rather contemporaneous to the growth of the stromatolites.

The phosphorites show marked compositional variation from carbonate apatite to carbonate fluorapatite and carbonate hydroxyl fluorapatite. The compositional variation with higher CaO/P_2O_5, CaO/MgO and CO_2/P_2O_5 ratio demonstrates the formation of phosphorite by replacement processes. The opposing behaviour of MgO with respect to CaO and P_2O_5 indicates replacement of dolomitic limestone/dolomite by calcium phosphate. Infra-red

spectral analysis indicates replacement of both the Ca and P position in phophate lattice by carbon. The fluorine content is thought to be fixed in the apatite structure in the early stage. The sympathetic relationship between F + OH and CO_2 indicates that CO_3F and/or CO_3OH might be substituted by PO_4 and vice versa. Hence it is reasonably concluded that CO_3^{2-} and OH^- are the principal substitution ions for PO_4^{3-}.

The dispersion pattern and behaviour of trace elements detected in the studied phosphorites and other associated rocks suggest that the fixation of Cu, Cr, Ni, Co, Li, Pb and Zn was more or less geochemically controlled by absorption on the surface of apatite or by the substitution in apatite lattice or the biogenic activity.

A genetic model of phosphorite depostis of Panchmahals have proposed which suggests that the role of geochemical environment in the deposition of the phosphorites as well as the accompanying activities of micro-organisms mutually interacted under a set of shallow intertidal to subtidal environmental conditions, lead one to believe that precipitation of phosphate was essentially dependent upon pH and Eh conditions, partial pressure of CO_2, temperature, replacement processes and ionic substitution. The presence of organic matter, association of carbonates, and limonitic dust and Fe_2O_3/FeO ratio suggest deposition of phosphorite in slightly reducing to fairly oxidizing environment. The various forms in which phosphorite occur appear to be related to some environmental changes at the time of deposition followed by some later structural disturbances.

CHAPTER-IX

SUMMARY AND CONCLUSION

The present investigation has been taken up to understand the mechanism and physico-chemical conditions in which the phosphorites of Panchmahals were formed. Considerable attention has been paid to study the geology, structure, mode of occurrence, stromatolitic assamblages, petromineralogy, geochemistry and genesis of these phosphorites.

The phosphorite deposits around Gandhra (22°27':73°41'31"), Panchmahals district, Gujarat are located within the thick succession of the Precambrian rocks belonging to the Champaner Group of the Aravalli Super Group. The phosphatic horizon is confined to the Khandia Formation of Champaner Group. The rock units encountered in the area of interest include metaconglomerate, quartzite, phyllites, dolomitic limestone, phosphorite, metagraywacke and granitoids occupying the entire southern and eastern part of the area. The general trend of the rock unit is NW-SE and dipping towards south and southwest at an angle of 45° in southern portion and 16° in northern portion of the area. The rocks around Gandhra form a major anticlinal fold with axial plane trending WNW-ESE to nearly E-W. The transverse fault in the area exhibits NNW-SSE and NNE-SSW trend. Three sets of joints viz., strike, dip and oblique joints were identified and recognised from the dolomitic limestone.

The rock units encountered in the area comprise mainly of dolomitic limestone, quartzites and phyllites which are the

product of low grade regional metamorphism and comparable with the low grade greenschist facies to chlorite schist facies.

The phosphorites of Panchmahals may be classified as follows:

i) Columnar algal stromatolitic phosphorite.

ii) Laminated algal stromatolitic phosphorite.

iii) Pelletal phosphorite.

iv) Nodular phosphorite

v) Bedded phosphorite

The phosphatic horizon is traceable over a strike length of about 0.40km in Chalvad block, 0.70km in Gandhra block, 0.40km in Ambapani block and 1.2km in Ranjitpura block with their horizontal width of 10 to 30 metres. The richest deposits (about 20% P_2O_5) is confined to the Ranjitpura block.

The presence of stromatolitic structures in these phosphorites and the presence of conglomeratic horizons at different stages indicate the shallow nature of the basin which is also stipulated by the presence of sedimentary structures such as laminations, current bedding and ripple marks. The repetitive sequence of conglomerate indicates that the basinal conditions were fluctuating. It has been suggested that, probably this represents a shallow epicontinental basin where mostly platform facies of sedimentation took place. A sharp decrease in thickness and even wedging out of the phosphorite bed in the direction of the strike indicates lacunae in sedimentation. It appears that the phosphorites have been formed in small

restricted depositional basins along the shallow regions of the sea and most likely in the tidal to intertidal regions where the algal stromatolites growing luxuriantly in a warm subaerial environment, precipitated and/or trapped phosphate minerals.

The various stromatolitic form species identified and recognised resemble to those of *Collenia columnaris, Collenia baicalica, Colonnella and Kussiella kusiensis*. These stromatolitic form species clearly indicate a shallow to very shallow depositional environment. These stromatolites when correlated with the world's stromatolites indicate the age of Champaner Group may fall between Lower Riphean to Upper Riphean which represent younger stratigraphic formation when compared with the Aravallis.

Petromineralogical studies indicate that carbonate apatite (dahllite) is the dominant phosphate mineral with some carbonate hydroxyl-fluorapatite and carbonate hydroxylapatite at places. Calcite and dolomite are the chief gangue mineral constituents of stromatolite bearing phosphorite. The other associated gangue minerals include quartz, feldspar, muscovite, sericite, tremolite, carbonaceous matter and opaques of iron oxides. The scanning electron microscopic study indicates that the mineral apatite form the hexagonal prisms and hexagonal pyramids. There are also obscure prisms and pyramids, altered and striped, growing in the early stage of growth. The growth of apatite grains in the calcite indicate the replacement of calcite by apatite.

Infra red spectral analyses of these phosphorites reveal the presence of structural CO_3 and OH ions in apatite structure. The discrete phase of CO_3 in these phosphorites is indicated by the presence of V_4 vibration in 710 cm^{-1} frequency region. The presence of a weak band in 650 cm^{-1} frequency region indicates the presence of hydroxyl apatite supported by the appearance of a weak peak in the 3500 cm^{-1} frequency region

Representative samples of phosphorites of Panchmahals were chemically analysed for the quantitative determination of their major oxides, viz. SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO, Mno, P_2O_5, FeO, Na_2O, K_2O, H_2O^+, CO_2 as well as F in terms of weight percent. The distribution of various chemical constituents show a wide variation in various lithological units of the area. Most common type of phosphorite in the study area are characterised by low to moderate concentration of P_2O_5, SiO_2, Fe_2O_3 and FeO, low concentration of MnO, Na_2O, K_2O, Al_2O_3, TiO_2, H_2O^+, and F and high concentration of CaO, MgO and CO_2. The sympathetic relationship between CaO and P_2O_5 indicates the formation of stable calcium phosphate. The presence of Mg^{2+} rather inhibits the growth of apatite crystallites. The strong negative relationship of MgO with CaO and P_2O_5 suggests the replacement of magnesian calcite by calcium phosphate. The excess water and sympathetic relationship of H_2O^+ with CaO/P_2O_5 ratio in few phosphorite samples suggest the possibility of PO_4 === $(OH)_4$ substitution. The sympathetic relationship of CO_2 with MgO while as antipathetic relation with CaO and P_2O_5 suggested that CO_2 in these phosphorite is a function of magnesian carbonate.

Moreover, with the entry of CO_2 in the apatite lattice Ca and P were partially replaced Furthermore, the sympathatic relationship of CO_2 with F as well as OH suggests the possiblity of substitution of CO_3F and/or CO_3OH by PO_4. Since majority of the samples have CaO/P_2O_5 ratios greater than 1.31, the most common substitution is that of PO_4^{3-} by CO_3^{2-}. The higher CaO/P_2O_5, CO_2/P_2O_5 ratios in these phosphorites also indicates the presence of carbonate apatite and the formation of phosphorite by replacement process of the constituents. Sympathetic relationship of F with P_2O_5 and F/P_2O^5 and F/H_2O ratios approach very near to carbonate hydroxyl fluorapatite. The negative relationship of F+OH with CO_2 suggest the manner of substitution might be $PO_4 \rightleftharpoons CO_3$; $PO_4 \rightleftharpoons (OH)_4$ and $F \rightleftharpoons OH$.

The principle oxides like SiO_2, Al_2O_3, TiO_2, K_2O etc. which are not related to apatite may have association with the silicate group. The high SiO_2/Al_2O_3 and low K_2O/Al_2O_3 ratios signify the presence of quartz and alumino-silicate minerals in these phosphorites. Furthermore, Fe_2O_3/FeO ratios suggest slightly reducing to fairly oxidizing environment of deposition of these phosphorites.

The trace elements such as Cu, Ni, Co, Pb, Zn, Cr, Sr, Rb, Li and Cd in the phosphorites and associated rocks were also determined quantitatively. Variable concentration of trace elements in the phosphorites has been influenced by various physico-chemical processess involved during weathering and leaching of the pre-existing rocks, and subsequently many of them

were assimilated to the sediments. The adsorption of some trace elements were mainly influenced by the principle absorbants like the phosphate minerals, some organic matter in addition to clay, iron and silicate minerals. The distribution, abundance and fixation of Cu, Ni, Co, Cr, Pb and Zn in the phosphate rocks is supposed to be controlled by the biogenic activity of fossil algae.

Sr and Pb are the elements which are susceptible to adsorption by phosphate minerals and the elements which are possibly adsorped by organic matter include Ni, Zn, Cr, Cu and Cd. Elements adsorbed by clay minerals include Li and Rb.

The pattern of trace elements distribution in these phosphorites and the geochemical behaviour of individual element suggests that most of the trace elements, that found their way into the ancient sediments, appear to have invaded the lattices of the phosphates, carbonates, silicates, and clay minerals and combined with them structurally.

The ingredients of phosphates are probably derived from -i) the pre-existing Banded Gneissic Complex as a result of their chemical decay followed by release of phosphorus to the shallow marine water and sediments ii) phytoplankton and other micro-organism also contributed some phosphorus. Marine upwelling caused the concentration of the phosphatic minerals over the shelf areas of a more or less restricted basin of deposition. The role of geochemical environment in the deposition of phosphorites as well as the accompanying activity of algal matter, that mutually interacted under a set of shallow

intertidal and shallow subtidal environmental condition leads one to conclude that precipitation of phosphate was essentially dependent upon pH and Eh conditions, partial pressure of CO_2, temperature, photosynthesis, replacement processes and biogenic activity. The various forms in which phosphorite occurs appear to be related to some environmental vicissitudes at the time of deposition followed by structural disturbances.

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EXPLANATION OF PLATES

Field Photographs

PLATE I

Fig.1 An outcrop of dolomitic limestone showing quartz veins (northern part of Gandhra, Panchmahals).

Fig.2 Discontinuous patches of stromatolitic phosphorites in barren dolomitic limestone (Chalvad block, Panchmahals).

PLATE II

Fig.1 Dolomitic limestone showing weathered, discontinuous bodies of stromatolitic phosphorites (Ambapani block).

Fig.2 Stromatolitic phosphorite showing intense weathering (Gandhra block, Panchmahals).

PLATE III

Fig.1 Columnar algal stromatolitic phosphorite (Baicalica species) (northern part of Gandhra).

Fig.2 Dolomitic limestone showing three sets of joints (north of Gandhra).

Fig.3 Laminated algal stromatolitic phosphorite (Collenia species) with barren dolomitic limestone (light), in north western part of Gandhra.

Photomicrographs of thin sections

PLATE IV

Fig.1 Photomicrograph showing the sericitization within dolomitic limestone of Gandhra block (+ nic., x 40).

Fig.2 Photomicrograph showing quartz grains coated with ferruginous matter in dolomitic limestone, Gandhra (+ nic., x 10).

PLATE V

Fig.1 Photomicrograph showing tremolite in the groundmass of phosphatic ferruginous dolomite, Gandhra (+ nic., x 10).

Fig.2 Photomicrograph showing quartz grains coated with ferruginous matter in quartzite, Gandhra (+ nic., x 10).

PLATE VI

Fig.1 Photomicrograph showing fine to medium grained collophane embedded in the calcareous groundmass of Ranjitpura block, Panchmahals (+ nic., x 3).

Fig.2 Photomicrograph showing alternate band of carbonate (light) and phosphate (dark) in stromatolitic phosphorites, Ranjitpura block, Panchmahals (+ nic., x 3).

Fig.3 Photomicrograph showing micaceous and ferruginous matter in phosphatic dolomite of Ranjitpura block, Panchmahals (+ nic., x 40).

Fig.4 Photomicrograph showing patches of phosphorites (isotropic) replacing carbonate material (light grey) in columnar stromatolitic phosphorite of Ranjitpura block, Panchmahals (+ nic., x 10).

PLATE VII

Fig.1 Photomicrograph showing the fibrous aggregates of tremolite in a calcareous matrix of Ranjitpura block (+ nic., x 10).

Fig.2 Photomicrograph showing fine to very fine grained collophane (dark) in the calcareous matrix of stromatolitic phosphorite of Ranjitpura block (+ nic., x 10).

Fig.3 Photomicrographic showing the partial replacement of dolomite by fine grained collophane (isotropic) in Ranjitpura block (+ nic., x 3).

Photomicrographs, using Scanning electron microscope

PLATE VIII

Fig.1 Hexagonal crystals of apatite having high content of phosphorus and containing some calcite in stromatolitic phosphorite of Ranjitpura block (SEM).

Fig.2 The superimposed growth phase of apatite in groundmass of calcite and dolomite of Ambapani block (SEM).

Fig.3 Calcite veins cross cutting collophane showing replacement of later by former (SEM).

PLATE IX

Fig.1 Apatitic molecular groups have aggregated in the grounmass of calcite showing the early stage of growth (SEM).

Fig.2 Hexagonal crystals of calcite in the barren stromatolitic dolomite of chalvad block (SEM).

Fig.3 Photomicrograph showing sericitization in the calcareous matrix of Gandhra block (SEM).

PLATE - 1

Fig. 1

Fig. 2

PLATE - II

Fig.1

Fig. 2

PLATE - III

Fig.1

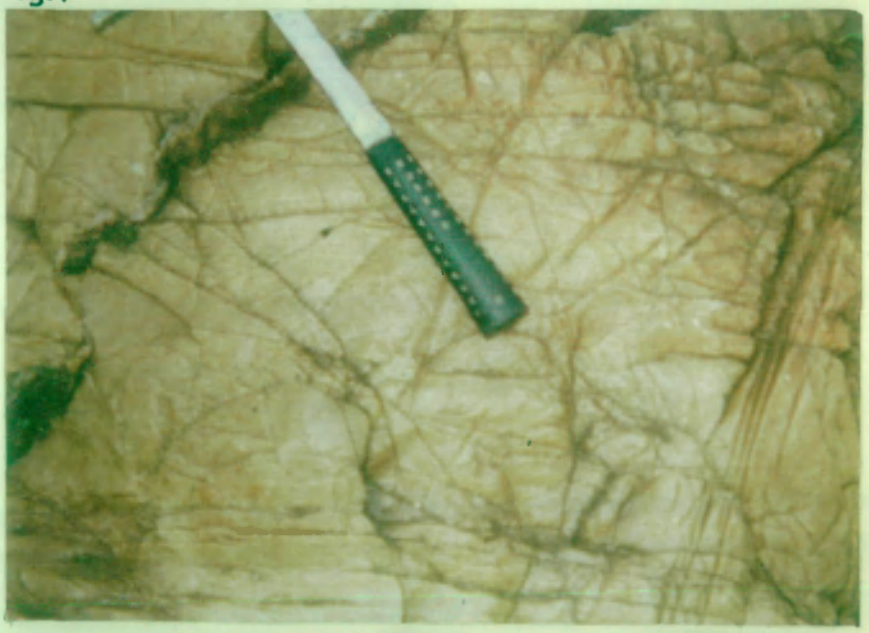


Fig.2

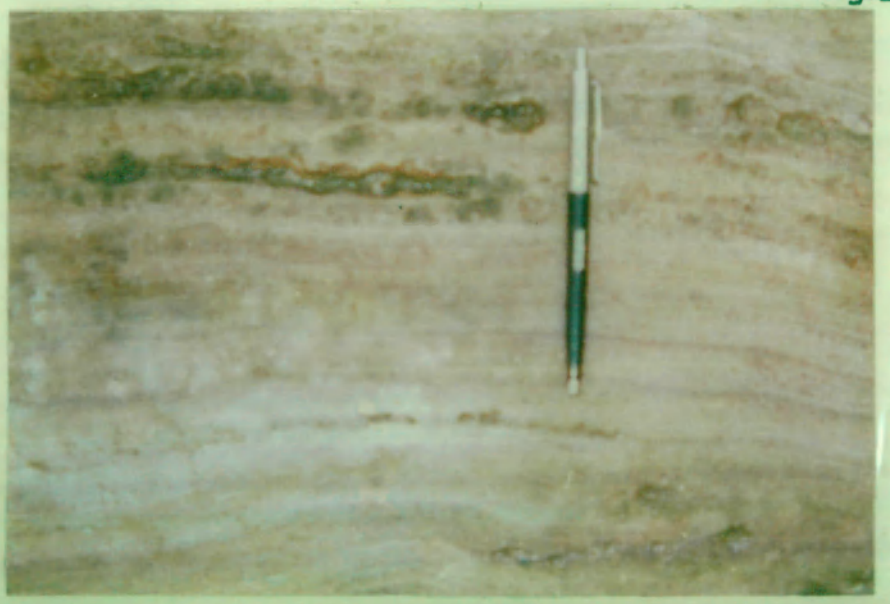
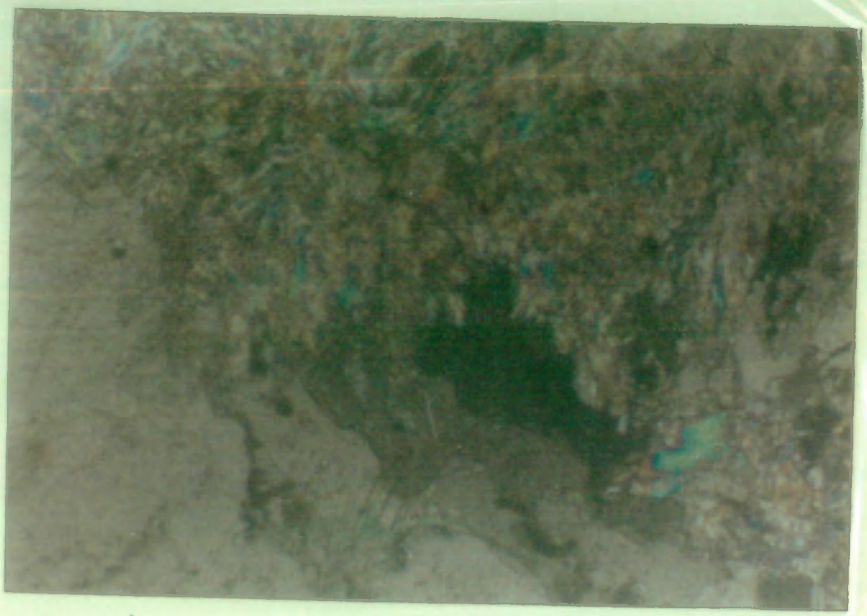


Fig. 3

PLATE IV



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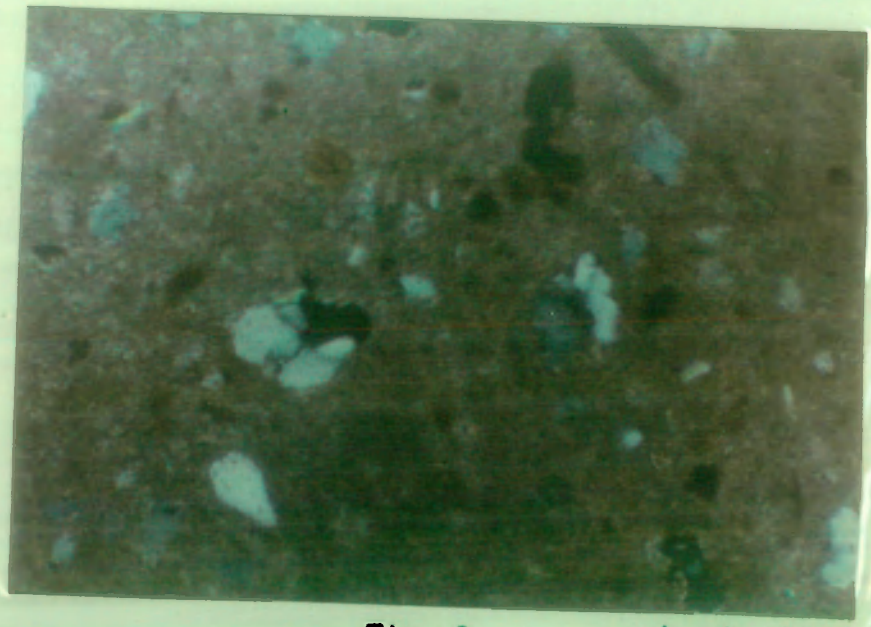

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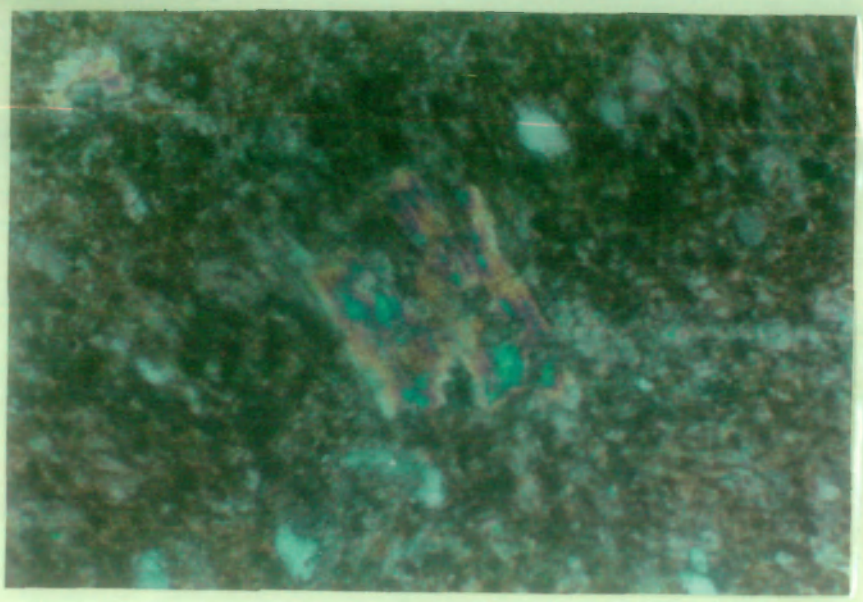
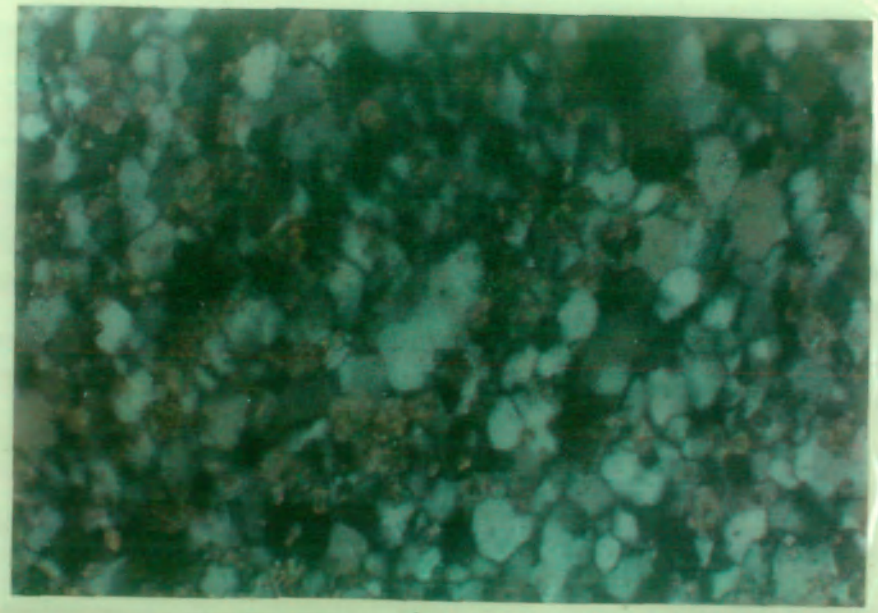


Fig. 1 (+nic., X10)



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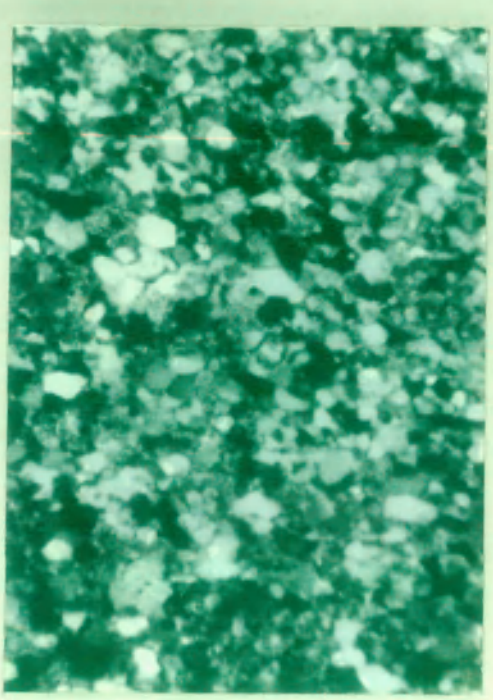

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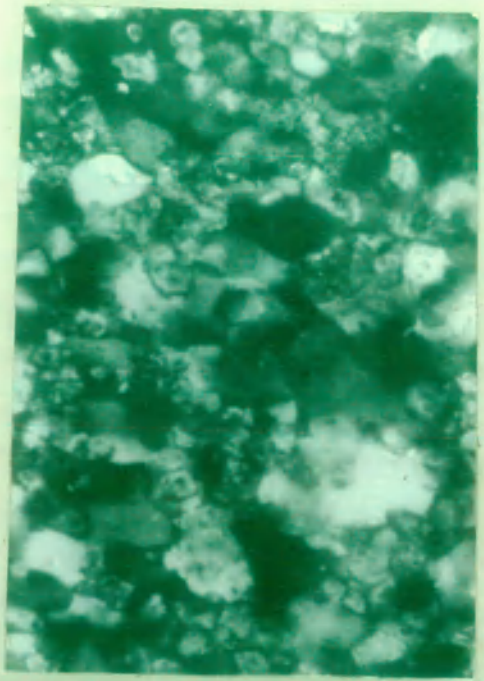
Fig. 2 (+nic., X3)



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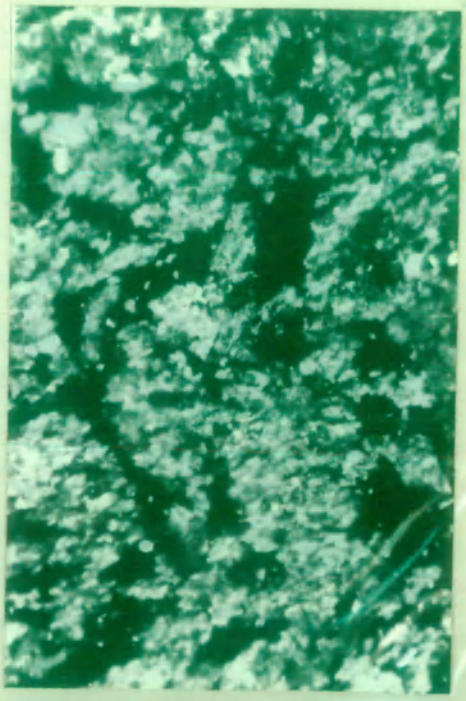
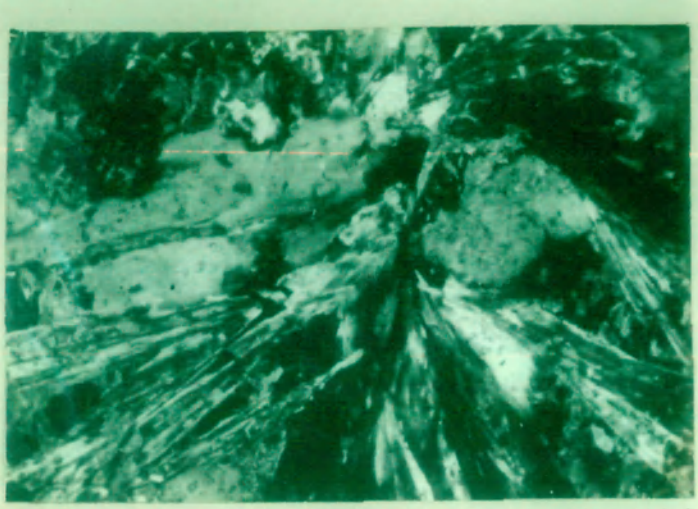


Fig. 4 (+nic., X10)

PLATE VII



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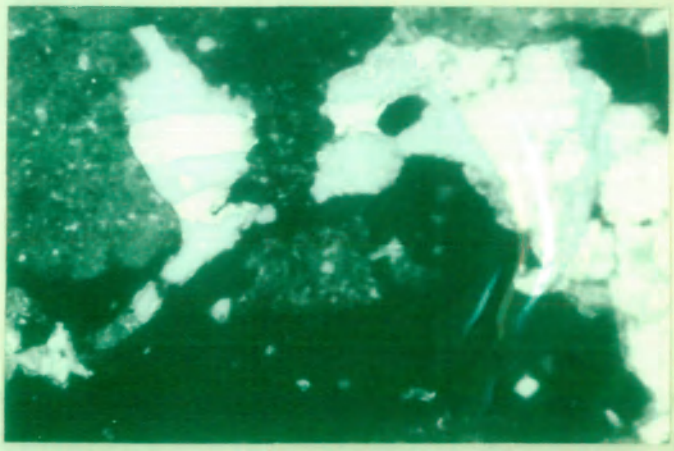

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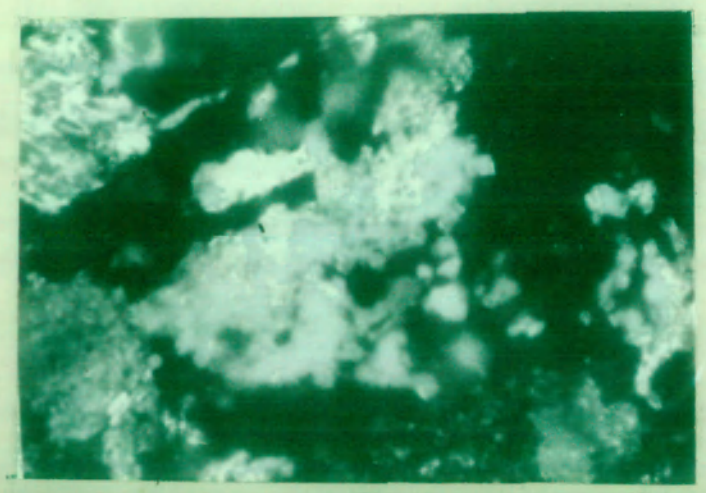


Fig. 3 (+nic.,X3)

PLATE VIII

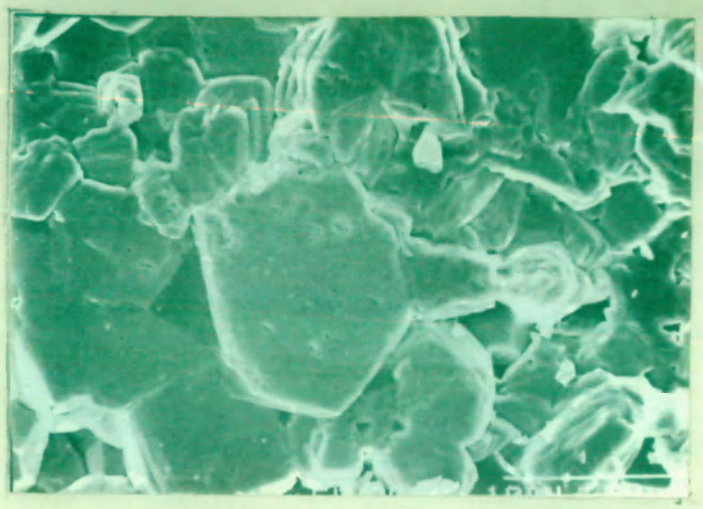
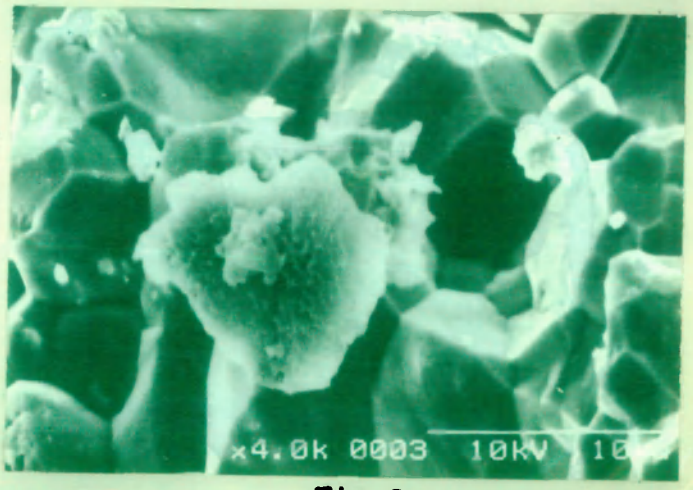


Fig. 1



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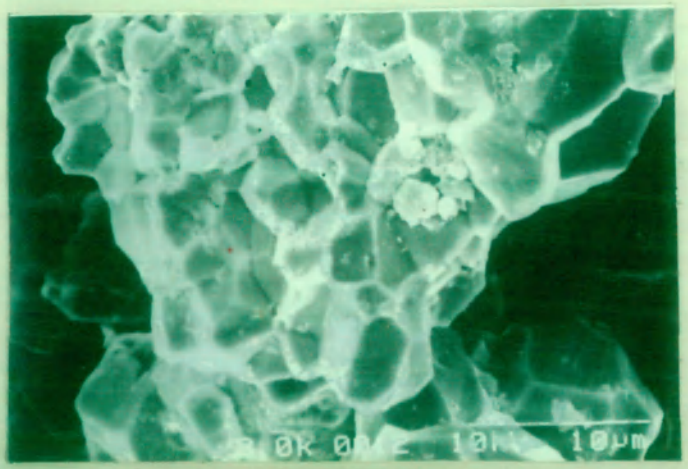

Fig. 3

PLATE IX

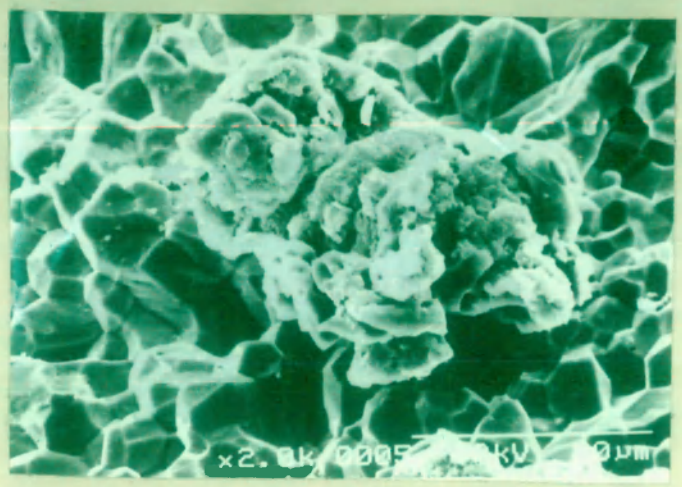

Fig. 1

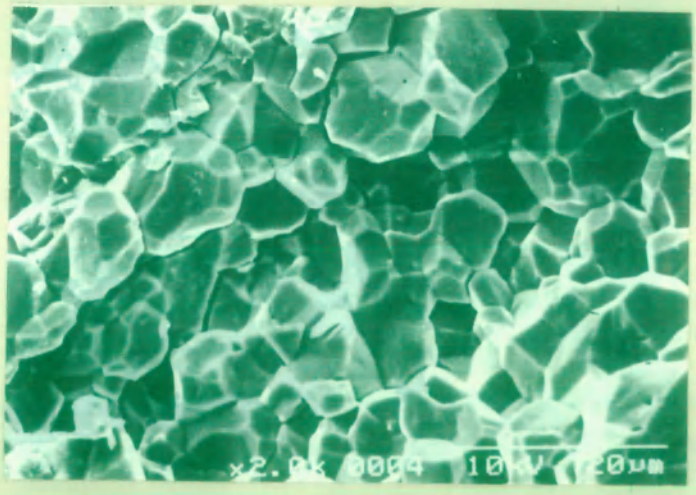

Fig. 2

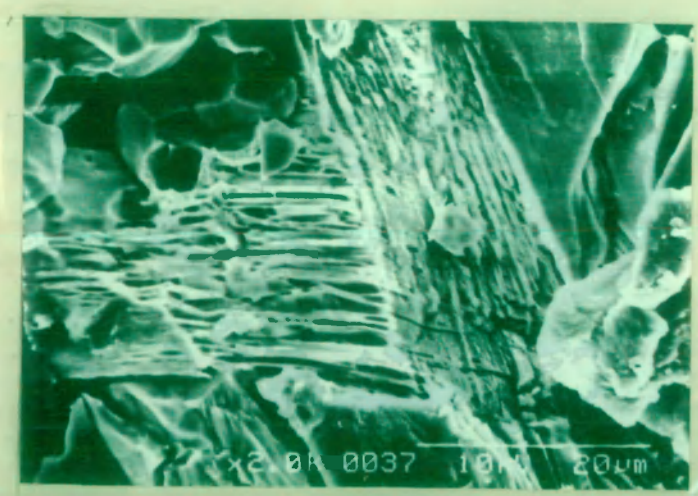

Fig. 3

APPENDIX

TABLE-III

Assignment of Infra red bands for $(PO_4)^{3-}$ ions of the samples

Sample	V_1	V_2	V_3	V_4
*Free $(PO_4)^{3-}$ ions	-	-	1080	600
*Hydroxyapatite (Synthetic)	959	-	1090,1025	628,602,563
*Fluorapatite (Synthetic)	964	-	1090,1036	740,602,575
*Carbonate apatite (Synthetic)	959	-	1090,1026	602,563
A	965	-	1090	670
B	935	-	1090,1020	670
C	959	-	1100,1020	670, 735

*Reference: Chakraborty, A.K. and Ghosh, S.K. 1960: Technology, Vol.3, p-149.

TABLE-IV

Assignment of Infra red bands for $(CO_3)^{2-}$ ions of the samples

Sample	V_1	V_2	V_3	V_4
*Free $(CO_3)^{-2}$ ions	-	879	1415	680
*Calcite	-	874	1430	710
*Aragonite	1080	866	1492	711,506
*Simple ionic Carbonates	1090,1020	890,820	1504,1470,1420	750,680
*Carbonate apatite (Synthetic)	-	872	1462,1411	-
*Francolite	-	865	1452	-
A	1090	874	1410	710
B	1020	880	1400,1430	716,670
C	1020	879	1410,1470	670,735,75

*Chaudhari, R. and Banerjee, K.C. 1967: Technology, Vol.3. p-97.

TABLE-V

Chemical composition of Chalvad phosphorites, Panchmahals district, Gujarat. (in wt. %)

	1	2	3	4	5	6	7	8	9	Mean
SiO_2	9.98	8.81	8.90	7.83	9.13	11.31	10.13	9.10	8.32	9.28
Al_2O_3	1.30	1.21	1.19	Tr.	1.24	1.43	1.39	1.31	0.98	1.12
TiO_2	0.58	0.52	Tr.	0.42	0.51	0.60	0.67	0.48	Tr.	0.42
Fe_2O_3	1.72	1.81	2.43	0.98	1.21	3.02	2.88	1.28	1.03	1.82
MnO	0.08	0.07	0.06	Tr.	0.06	0.11	0.09	0.05	Tr.	0.06
CaO	40.36	48.30	43.90	49.31	42.08	41.00	42.81	44.36	48.36	44.50
MgO	11.00	7.10	8.37	7.00	10.31	9.81	8.82	8.81	7.40	8.74
P_2O_5	5.64	7.81	6.84	8.90	6.22	4.80	5.18	6.42	7.34	6.57
FeO	1.82	1.49	0.89	1.80	1.23	1.01	1.83	2.05	2.60	1.64
Na_2O	0.36	0.42	0.61	0.69	ND	0.44	0.38	0.38	0.13	0.38
K_2O	0.21	0.30	0.52	0.72	0.80	0.45	0.36	ND	0.20	0.40
H_2O^+	0.72	0.88	0.46	0.91	0.63	0.41	0.50	0.39	0.61	0.61
CO_2	26.50	22.08	24.70	21.30	24.70	27.00	25.19	24.91	23.00	24.38
F	ND	0.63	0.54	0.70	0.34	ND	ND	0.41	0.62	0.36
Total	100.29	101.43	99.41	100.56	98.46	101.39	100.23	99.95	100.59	

TABLE-VI

Chemical composition of Gandhra phosphorites, Panchmahals district, Gujarat. (in wt. %)

	10	11	12	13	14	15	16	17	18	19	20	21	22	23	Mean
SiO_2	9.70	8.09	6.39	7.73	4.67	10.40	8.40	7.09	3.40	3.37	2.70	4.29	7.05	6.21	6.39
Al_2O_3	1.45	1.13	1.56	1.35	1.13	1.43	1.35	1.33	1.50	1.33	0.98	1.55	1.38	1.33	1.34
TiO_2	0.35	0.27	0.30	0.41	0.80	0.53	0.61	0.33	0.35	0.42	0.37	0.66	0.62	0.58	0.47
Fe_2O_3	1.65	1.42	2.01	1.00	2.06	2.99	2.95	0.63	1.07	0.58	1.10	1.02	2.00	1.62	1.58
MnO	0.08	0.04	0.03	0.08	0.02	0.04	0.07	0.04	0.04	0.07	0.08	0.12	0.08	0.06	0.06
CaO	42.46	53.29	48.09	42.91	48.71	37.76	47.05	46.16	58.19	54.99	43.74	47.91	46.60	47.80	47.59
MgO	10.89	5.58	4.28	6.92	3.80	7.40	5.74	7.32	3.15	8.73	10.08	9.48	7.81	7.10	7.02
P_2O_5	8.17	11.78	6.35	5.26	6.17	4.87	7.48	10.70	9.18	10.74	10.69	7.07	6.98	8.08	8.11
FeO	0.64	0.12	0.56	2.24	0.80	3.44	2.68	4.76	2.00	2.28	3.48	4.20	1.81	2.16	2.23
Na_2O	0.78	0.86	0.55	0.22	1.16	0.40	0.25	0.44	0.31	0.51	0.81	1.06	0.81	0.82	0.64
K_2O	0.30	0.91	0.42	0.25	0.35	0.56	1.02	0.04	0.24	0.12	0.09	0.08	0.19	0.23	0.34
H_2O^+	0.74	0.66	0.64	0.42	0.50	0.88	0.62	0.70	0.71	0.91	0.72	0.85	0.88	1.01	0.73
CO_2	22.30	15.51	27.72	29.41	29.13	28.35	21.18	19.66	17.86	15.26	24.90	23.06	24.10	21.24	22.81
F	0.80	1.10	0.64	Tr.	Tr.	ND	0.88	1.00	0.82	1.01	1.04	ND	ND	0.80	0.58
Total	100.31	100.76	99.54	98.20	99.30	99.05	100.28	100.20	98.82	100.32	100.48	101.35	100.31	99.04	

TABLE-VII

Chemical composition of Ambapani phosphorites, Panchmahals district, Gujarat. (in wt. %)

	24	25	26	27	28	29	30	31	32	Mean
SiO_2	6.62	7.82	10.81	7.78	9.73	5.68	6.98	8.86	7.91	8.02
Al_2O_3	0.99	1.19	1.41	1.32	1.38	0.96	0.98	1.34	0.89	1.16
TiO_2	0.20	0.51	0.63	Tr.	0.63	0.58	ND	0.64	0.44	0.40
Fe_2O_3	1.21	3.41	1.91	2.68	1.92	2.00	0.79	2.02	1.93	1.99
MnO	0.06	0.09	0.07	0.08	0.04	0.08	0.04	0.07	0.06	0.06
CaO	47.81	42.28	40.32	41.85	45.83	44.58	46.60	42.30	43.40	43.88
MgO	7.81	9.83	11.90	9.95	7.81	10.70	8.58	9.20	10.21	9.55
P_2O_5	7.78	4.19	3.89	4.18	6.10	5.88	8.62	4.28	5.92	5.65
FeO	2.01	1.81	0.81	1.80	0.93	1.83	2.21	1.01	1.27	1.52
Na_2O	0.83	0.61	0.26	0.62	1.00	0.88	0.91	0.46	0.61	0.61
K_2O	0.42	0.83	1.10	0.90	0.61	0.80	0.31	0.81	0.62	0.71
H_2O^+	1.01	0.72	0.61	0.68	0.93	0.61	0.98	0.62	0.67	0.76
CO_2	22.02	26.12	27.90	26.90	23.80	24.18	21.83	27.75	25.90	25.16
F	0.61	0.23	Tr.	0.32	Tr.	0.43	0.80	0.31	0.56	0.36
Total	99.38	99.64	101.62	100.06	100.71	99.19	99.05	99.61	100.39	

TABLE-VIII

Chemical composition of Ranjitpura phosphorites, Panchmahals district, Gujarat. (in wt. %)

	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	Mean
SiO_2	8.85	8.5	9.87	6.8	4.88	5.30	8.18	5.26	6.66	4.32	5.01	10.11	6.30	8.28	5.84	4.80	5.82	4.33	6.62
Al_2O_3	1.43	1.41	1.58	1.31	0.96	1.32	1.41	0.94	1.36	0.91	0.92	1.50	1.10	1.30	1.12	Tr.	1.22	0.69	1.14
TiO_2	0.34	0.46	0.60	0.31	Tr.	0.34	Tr.	0.24	0.27	0.21	Tr.	0.51	0.22	0.36	0.26	0.20	0.30	Tr.	0.26
Fe_2O_3	1.78	3.01	2.67	1.28	0.98	1.06	1.89	1.21	1.38	0.88	0.93	2.0	1.33	2.06	0.86	1.12	1.24	1.27	1.50
MnO	0.08	0.08	0.07	0.05	0.03	0.05	0.06	0.05	0.05	Tr.	0.04	0.10	0.06	0.07	0.07	0.03	0.05	0.03	0.05
CaO	43.51	42.50	41.70	43.00	47.12	46.31	42.60	46.30	42.38	45.14	44.2	40.82	43.78	40.7	43.38	43.71	43.10	44.10	43.57
MgO	10.11	9.08	8.80	8.31	9.58	7.51	8.88	7.38	9.08	10.23	8.71	11.08	7.91	10.0	6.84	7.11	8.21	8.14	8.72
P_2O_5	11.01	12.00	9.87	13.22	14.07	13.98	11.70	15.25	13.63	17.73	16.86	8.78	15.85	13.10	16.78	20.11	15.10	19.65	14.38
FeO	1.03	0.91	1.37	1.29	2.31	2.37	1.22	1.27	1.10	2.11	1.69	0.92	0.82	1.0	1.79	2.0	2.13	1.10	1.52
Na_2O	0.23	0.57	0.26	0.19	0.82	0.79	0.68	0.61	0.77	0.76	0.61	0.71	0.77	0.68	0.80	0.93	0.70	0.91	0.65
K_2O	0.41	0.62	0.40	0.68	0.44	0.62	0.81	0.54	0.43	0.32	0.43	0.57	0.44	0.57	0.48	Tr.	0.51	Tr.	0.46
H_2O^+	1.00	0.90	0.98	0.87	0.81	0.96	0.82	1.10	0.92	0.86	0.91	0.41	1.16	1.10	0.98	1.06	0.94	1.20	0.94
CO_2	20.6	20.1	21.82	20.9	20.16	19.87	20.98	19.81	20.98	15.61	18.22	22.50	18.31	21.04	19.0	15.13	19.8	15.88	19.48
F	ND	0.81	0.68	0.91	0.86	0.81	0.72	0.84	0.81	1.01	0.89	ND	0.81	0.64	0.92	1.02	0.92	1.00	0.76
Total	100.36	100.95	100.67	99.12	102.21	101.29	99.95	100.8	99.82	100.09	99.42	100.01	98.86	100.91	99.12	97.22	100.04	98.30	

TABLE-IX

Minimum, Maximum, Average values and Standard deviation of major oxides for phosphorites of Chalvad, Gandhra, Ambapani and Ranjitpura blocks, Panchmahals.

Major	Chalvad Phosphorites				Gandhra Phosphorites				Ambapani Phosphorites				Ranjitpura Phosphorites			
Oxides	Min.	Max.	Aver.	S.D.	Min.	Max.	Aver.	S.D.	Min.	Max.	Aver.	S.D.	Min.	Max.	Aver.	S.D.
SiO_2	7.83	11.31	9.28	1.05	2.70	10.40	6.39	2.41	5.68	10.81	8.02	1.58	4.32	10.11	6.62	1.84
Al_2O_3	Tr.	1.43	1.12	0.44	0.98	1.56	1.34	0.20	0.89	1.41	1.16	0.21	Tr.	1.58	1.14	0.36
TiO_2	Tr.	0.67	0.42	0.25	0.27	0.80	0.47	0.16	Tr.	0.64	0.40	0.27	Tr.	0.60	0.26	0.17
Fe_2O_3	0.98	3.02	1.82	0.79	0.58	2.99	1.58	0.76	0.79	3.41	1.99	0.76	0.86	3.01	1.50	0.60
MnO	Tr.	0.11	0.06	0.04	0.02	012	0.06	0.03	0.04	0.09	0.06	0.02	Tr.	0.10	0.05	0.23
CaO	40.36	49.31	44.50	3.37	37.76	58.19	47.54	3.29	40.32	47.81	43.88	2.48	40.70	47.12	43.57	1.73
MgO	7.00	11.00	8.74	1.43	3.15	10.89	7.02	2.33	7.81	11.90	9.55	1.35	6.94	11.08	8.72	1.13
P_2O_5	4.80	8.90	6.57	1.31	5.26	11.78	8.11	2.20	3.89	8.62	5.65	1.69	8.78	20.11	14.38	3.05
FeO	0.89	2.60	1.64	0.54	0.12	4.76	2.23	1.40	0.81	2.21	1.52	0.52	0.82	2.37	1.52	0.51
Na_2O	Tr.	0.69	0.38	0.21	0.22	1.16	0.64	0.30	0.26	1.00	0.69	0.24	0.19	0.93	0.65	0.25
K_2O	Tr.	0.80	0.40	0.26	0.04	1.02	0.34	0.30	0.31	1.10	0.71	0.25	Tr.	0.81	0.46	0.20
H_2O^+	0.39	0.91	0.61	0.19	0.42	1.01	0.73	0.16	0.61	1.01	0.76	0.17	0.41	1.12	0.94	0.25
CO_2	21.3	27.0	24.38	1.91	15.51	29.41	22.81	4.75	21.83	27.90	25.16	2.30	15.13	22.50	19.48	0.17
F	Tr.	0.70	0.36	0.29	Tr.	1.10	0.58	0.46	Tr.	0.80	0.36	0.27	Tr.	1.02	0.76	2.06

* Aver. = Average; **S.D. = Standard Deviation.

TABLE-X

Chemical composition of various rocks associated with phosphorites of Panchmahals district, Gujarat (in wt. %)

	Dolomitic limestone				Quartzites				Phyllites		
	DL-1	DL-2	DL-3	Mean	Q-1	Q-2	Q-3	Mean	P-1	P-2	Mean
SiO_2	6.81	7.08	5.01	6.30	82.21	84.30	85.57	84.03	56.71	55.50	56.01
Al_2O_3	0.98	1.21	0.78	0.99	2.11	2.88	2.48	2.49	13.81	14.86	14.33
TiO_2	ND	0.21	0.12	0.11	Tr	0.23	Tr	0.08	0.91	0.43	0.67
Fe_2O_3	0.98	1.87	1.31	1.39	3.26	3.71	4.07	3.68	4.36	3.92	4.14
MnO	0.06	0.09	0.11	0.09	0.08	0.06	0.13	0.09	0.11	0.15	0.13
CaO	43.00	41.14	40.51	41.55	3.71	3.81	2.89	3.47	3.13	2.79	2.96
MgO	8.01	7.48	9.00	8.16	1.02	1.12	1.21	1.12	2.48	2.72	2.60
P_2O_5	0.04	0.05	0.41	0.17	0.08	0.50	0.37	0.32	Tr.	ND	Tr.
FeO	1.01	1.26	1.70	1.32	2.11	1.68	2.52	2.10	2.31	1.54	1.92
Na_2O	0.04	Tr.	0.21	0.08	0.26	0.43	0 42	0.37	0.41	0.62	0.51
K_2O	0.06	ND	0.16	0.07	0.29	0.39	0.33	0.34	1.11	1.72	1.41
H_2O^+	0.20	0.34	0.30	0.28	0.86	0.56	0.74	0.72	4.48	4.89	4.68
CO_2	40.22	39.60	41.44	40.42	1.12	1.18	0.68	0.99	9.02	9.74	9.38
F	ND	ND	0.12	0.04	ND	ND	ND	ND	Tr.	ND	ND
	101.41	100.33	101.08		97.71	100.85	101.31		98.84	98.88	

TABLE-XI

SiO_2/Al_2O_3, MgO/Al_2O_3, K_2O/Al_2O_3, Fe_2O_3/Al_2O_3, Al_2O_3/TiO_2, Fe_2O_3/FeO, CaO/P_2O_5, Ca/Mg, CO_2/P_2O_5 and F/P_2O_5 ratios for Chalvad phosphorites, Panchmahals, Gujarat.

S.No.	SiO_2/Al_2O_3	MgO/Al_2O_3	K_2O/Al_2O_3	Fe_2O_3/Al_2O_3	Al_2O_3/TiO_2	Fe_2O_3/FeO	CaO/P_2O_5	Ca/Mg	CO_2/P_2O_5	F/P_2O_5
1	7.68	8.46	0.16	1.32	2.24	0.95	7.16	4.35	4.70	-
2	7.28	5.87	0.25	1.50	2.33	1.21	6.18	8.06	2.83	0.08
3	7.48	7.03	0.44	2.04	-	2.73	6.42	6.21	3.61	0.08
4	-	-	-	-	-	0.54	5.54	8.35	2.39	0.08
5	7.36	8.31	0.65	0.97	2.43	0.98	6.77	4.83	3.97	0.05
6	7.91	6.86	0.31	2.11	2.38	2.99	8.54	4.95	5.63	-
7	7.29	6.35	0.26	2.07	2.07	1.57	8.26	5.75	4.86	-
8	6.95	6.73	-	0.98	2.73	0.62	6.91	5.97	3.88	0.06
9	8.49	7.55	0.20	1.05	-	0.40	6.59	7.75	3.13	0.08

TABLE-XII

SiO_2/Al_2O_3, MgO/Al_2O_3, K_2O/Al_2O_3, Fe_2O_3/Al_2O_3, Al_2O_3/TiO_2, Fe_2O_3/FeO, CaO/P_2O_5, Ca/Mg, CO_2/P_2O_5 and F/P_2O_5 ratios for Gandhra phosphorites, Panchmahals, Gujarat.

S.No.	SiO_2/Al_2O_3	MgO/Al_2O_3	K_2O/Al_2O_3	Fe_2O_3/Al_2O_3	Al_2O_3/TiO_2	Fe_2O_3/FeO	CaO/P_2O_5	Ca/Mg	CO_2/P_2O_5	F/P_2O_5
10	6.69	7.51	0.21	1.13	4.14	2.57	5.19	4.62	2.73	0.10
11	7.15	4.93	0.81	1.25	4.18	11.83	4.52	11.30	1.31	0.09
12	4.09	2.74	0.27	1.28	5.20	3.58	7.57	13.32	4.36	0.10
13	5.72	5.12	0.19	0.74	3.29	0.45	8.15	7.35	5.59	-
14	4.13	3.36	0.31	1.82	1.41	2.57	7.89	15.20	4.72	-
15	7.27	5.17	0.39	2.09	2.50	0.87	7.75	6.05	5.82	-
16	6.22	4.25	0.76	2.18	2.21	1.10	6.29	9.72	2.83	0.12
17	5.33	5.50	0.03	0.47	4.03	0.13	4.31	7.48	1.83	0.09
18	2.27	2.18	0.16	0.71	4.28	0.53	6.34	21.89	1.94	0.09
19	2.53	6.56	0.09	0.44	3.17	0.18	5.12	7.46	1.42	0.09
20	2.75	10.28	0.09	0.12	2.64	0.32	4.09	5.14	2.30	0.10
21	2.76	6.12	0.05	0.66	2.34	0.24	6.78	5.99	3.26	-
22	5.11	5.66	0.14	1.45	2.22	1.10	6.68	7.07	3.45	-
23	4.67	5.34	0.17	1.22	2.29	0.75	5.92	7.98	2.63	0.10

TABLE-XIII

SiO_2/Al_2O_3, MgO/Al_2O_3, K_2O/Al_2O_3, Fe_2O_3/Al_2O_3, Al_2O_3/TiO_2, Fe_2O_3/FeO, CaO/P_2O_5, Ca/Mg, CO_2/P_2O_5 and F/P_2O_5 ratios for Ambapani phosphorites, Panchmahals, Gujarat.

S.No.	SiO_2/Al_2O_3	MgO/Al_2O_3	K_2O/Al_2O_3	Fe_2O_3/Al_2O_3	Al_2O_3/TiO_2	Fe_2O_3/FeO	CaO/P_2O_5	Ca/Mg	CO_2/P_2O_5	F/P_2O_5
24	6.69	7.89	0.42	1.22	4.95	0.60	6.15	7.25	2.83	0.08
25	6.57	8.26	0.70	2.87	2.33	1.88	10.09	5.10	6.23	0.05
26	7.67	8.44	0.78	1.35	2.24	2.36	10.37	4.01	7.17	-
27	5.89	7.54	0.68	2.03	-	1.49	10.01	4.98	6.43	0.08
28	7.05	5.66	0.46	1.45	2.19	2.06	7.51	6.95	3.90	-
29	5.92	11.15	0.83	2.08	1.66	1.09	7.58	4.94	4.11	0.07
30	7.12	8.76	0.32	0.81	-	0.36	5.41	6.44	2.53	0.09
31	6.61	6.87	0.61	1.53	2.09	2.00	9.88	5.45	6.48	0.07
32	8.89	11.47	0.70	2.17	2.02	1.52	7.33	5.04	4.38	0.09

TABLE-XIV

SiO_2/Al_2O_3, MgO/Al_2O_3, K_2O/Al_2O_3, Fe_2O_3/Al_2O_3, Al_2O_3/TiO_2, Fe_2O_3/FeO, CaO/P_2O_5, Ca/Mg, CO_2/P_2O_5 and F/P_2O_5 ratios for Ranjitpura phosphorites, Panchmahals, Gujarat.

S.No.	SiO_2/Al_2O_3	MgO/Al_2O_3	K_2O/Al_2O_3	Fe_2O_3/Al_2O_3	Al_2O_3/TiO_2	Fe_2O_3/FeO	CaO/P_2O_5	Ca/Mg	CO_2/P_2O_5	F/P_2O_5
33	6.18	7.07	0.28	1.24	4.47	1.73	3.95	5.10	1.87	-
34	6.03	6.44	0.44	2.13	3.06	3.31	3.54	5.54	1.67	0.06
35	6.25	5.57	0.25	1.69	2.60	1.95	4.22	5.61	2.20	0.07
36	5.19	6.34	0.52	0.97	4.22	0.99	3.25	6.13	1.58	0.07
37	5.08	9.98	0.46	1.02	-	0.42	3.35	5.83	1.43	0.06
38	4.02	5.69	0.47	0.80	3.88	0.44	3.31	7.31	1.42	0.05
39	5.80	6.29	0.57	1.34	-	1.55	3.64	5.68	1.79	0.06
40	5.59	7.85	0.57	1.28	3.91	0.95	3.04	7.43	1.29	0.05
41	4.89	6.67	0.31	1.01	5.03	1.25	3.11	5.53	1.54	0.06
42	4.74	11.24	0.35	0.96	4.33	0.41	2.54	5.23	0.88	0.06
43	5.44	9.46	0.46	1.01	-	0.55	2.62	6.41	1.08	0.05
44	6.74	7.38	0.38	1.33	2.94	2.17	4.65	4.37	2.56	-
45	5.67	7.12	0.39	1.19	5.04	0.73	2.76	6.56	1.15	0.05
46	6.36	7.69	0.44	1.58	3.61	2.06	3.11	4.82	1.60	0.05
47	5.21	6.19	0.43	0.77	4.30	0.48	2.58	7.40	1.13	0.05
48	4.80	-	-	-	-	0.56	2.17	7.28	0.75	0.05
49	4.77	6.73	0.42	1.01	4.06	0.58	2.85	6.22	1.31	0.06
50	6.27	11.79	-	1.84	-	1.15	2.24	6.42	0.81	0.05

TABLE-XV

CaO/MgO, Na_2O/K_2O, MnO/CaO, Fe/P_2O_5, F/H_2O^+, CO_2/H_2O^+, H_2O^+/CO_2 and Mn/Fe ratios for Chalvad phosphorites, Panchmahals, Gujarat.

S.No.	CaO/MgO	Na_2O/K_2O	MnO/CaO	Fe/P_2O_5	F/H_2O^+	CO_2/H_2O^+	H_2O^+/CO_2	Mn/Fe
1	3.67	1.71	1.98×10^{-3}	0.21	-	36.80	0.03	0.051
2	6.80	1.40	1.45×10^{-3}	0.16	0.72	25.09	0.04	0.043
3	5.25	1.17	1.37×10^{-3}	0.25	1.17	53.70	0.02	0.027
4	7.04	6.96	-	0.08	0.77	23.41	0.04	-
5	4.08	-	1.43×10^{-3}	0.13	0.54	39.21	0.03	0.055
6	4.18	0.98	2.68 x 10-3	0.44	-	65.85	0.02	0.040
7	4.85	1.06	2.10×10^{-3}	0.39	-	50.38	0.02	0.035
8	5.03	-	1.13×10^{-3}	0.14	1.05	63.87	0.02	0.043
9	6.54	0.65	-	0.10	1.02	37.70	0.03	-

TABLE-XVI

CaO/MgO, Na_2O/K_2O, MnO/CaO, Fe/P_2O_5, F/H_2O^+, CO_2/H_2O^+, H_2O^+/CO_2 and Mn/Fe ratios for Gandhra phosphorites, Panchmahals, Gujarat.

S.No.	CaO/MgO	Na_2O/K_2O	MnO/CaO	Fe/P_2O_5	F/H_2O^+	CO_2/H_2O^+	H_2O^+/CO_2	Mn/Fe
10	3.89	2.60	1.88×10^{-3}	0.14	1.08	30.13	3.3×10^{-2}	0.054
11	9.55	0.95	0.75×10^{-3}	0.80	1.67	23.50	4.2×10^{-2}	0.031
12	11.23	1.31	0.62×10^{-3}	0.22	1.00	43.31	2.3×10^{-2}	0.017
13	6.21	0.88	7.8×10^{-3}	0.13	-	70.02	1.4×10^{-2}	0.088
14	12.82	3.31	0.41×10^{-3}	0.23	-	58.26	1.7×10^{-2}	0.011
15	5.10	0.71	1.06×10^{-3}	0.43	-	32.22	3.1×10^{-2}	0.015
16	8.19	0.25	1.49×10^{-3}	0.28	1.42	34.16	2.9×10^{-2}	0.026
17	6.31	11.00	0.87×10^{-3}	0.04	1.43	28.08	3.5×10^{-2}	0.070
18	18.5	1.29	0.69×10^{-3}	0.08	1.15	25.15	3.9×10^{-2}	0.041
19	6.29	4.25	1.27×10^{-3}	0.04	1.11	16.77	5.9×10^{-2}	0.133
20	4.33	2.00	1.83×10^{-3}	0.07	1.14	34.16	2.9×10^{-2}	0.088
21	5.05	13.25	2.50×10^{-3}	0.10	-	27.13	3.6×10^{-2}	0.13
22	5.97	4.26	1.72×10^{-3}	0.20	-	27.39	3.6×10^{-2}	0.044
23	6.73	3.56	1.25×10^{-3}	0.14	0.79	21.03	4.7×10^{-2}	0.041

TABLE-XVII

CaO/MgO, Na_2O/K_2O, MnO/CaO, Fe/P_2O_5, F/H_2O^+, CO_2/H_2O^+, H_2O^+/CO_2 and Mn/Fe ratios for Ambapani phosphorites, Panchmahals, Gujarat.

S.No.	CaO/MgO	Na_2O/K_2O	MnO/CaO	Fe/P_2O_5	F/H_2O^+	CO_2/H_2O^+	H_2O^+/CO_2	Mn/Fe
24	6.12	1.98	1.25×10^{-3}	0.11	0.60	21.8	0.05	0.055
25	4.30	0.73	2.13×10^{-3}	0.57	0.32	36.28	0.03	0.029
26	3.39	0.24	1.70×10^{-3}	0.34	-	45.73	0.02	0.041
27	4.21	0.69	1.91×10^{-3}	0.45	0.47	39.56	0.03	0.033
28	5.87	1.64	0.87×10^{-3}	0.22	-	25.59	0.04	0.023
29	4.17	1.10	1.79×10^{-3}	0.24	0.70	39.64	0.03	0.044
30	5.43	2.94	0.86×10^{-3}	0.06	0.82	22.28	0.04	0.056
31	4.60	0.57	1.65×10^{-3}	0.33	0.50	44.76	0.02	0.038
32	4.25	0.98	1.38×10^{-3}	0.23	0.84	38.66	0.03	0.034

TABLE-XVIII

CaO/MgO, Na_2O/K_2O, MnO/CaO, Fe/P_2O_5, F/H_2O^+, CO_2/H_2O^+, H_2O^+/CO_2 and Mn/Fe ratios for Ranjitpura phosphorites, Panchmahals, Gujarat.

S.No.	CaO/MgO	Na_2O/K_2O	MnO/CaO	Fe/P_2O_5	F/H_2O^+	CO_2/H_2O^+	H_2O^+/CO_2	Mn/Fe
33	4.30	0.56	0.002	-	-	20.60	0.05	0.050
34	4.68	0.92	0.002	0.06	0.9	22.33	0.04	0.029
35	4.74	0.65	0.001	0.07	0.69	22.26	0.04	0.029
36	5.17	0.26	0.001	0.07	1.04	24.02	0.04	0.035
37	4.91	1.86	0.001	0.06	1.06	24.88	0.04	0.034
38	6.17	1.77	0.001	0.05	0.84	20.69	0.05	0.042
39	4.79	0.84	0.001	0.06	0.87	25.58	0.04	0.035
40	6.27	1.13	0.001	0.05	0.76	18.01	0.05	0.037
41	4.66	1.79	0.001	0.06	0.88	22.80	0.04	0.032
42	4.41	2.37	-	0.06	1.17	18.15	0.05	-
43	5.07	1.42	0.009	0.05	0.98	20.02	0.05	0.048
44	3.68	1.24	0.02	-	-	54.88	0.02	0.055
45	5.53	1.75	0.001	0.05	0.69	15.74	0.06	0.050
46	4.07	1.19	0.002	0.05	0.58	19.12	0.05	0.038
47	6.25	1.66	0.001	0.05	0.94	19.38	0.05	0.090
48	6.15	-	0.001	0.05	1.02	15.13	0.07	0.030
49	5.25	1.37	0.001	0.06	0.98	21.06	0.05	0.045
50	5.42	-	0.001	0.05	0.83	13.23	0.08	0.026

TABLE-XIX

Recalculated to 100 wt.% of the bulk components of (A) $CaO-MgO-P_2O_5$ (B) $CaO-MgO-SiO_2$ and (C) $CaO-MgO-CO_2$ in Chalvad phosphorites

	(A)			(B)			(C)		
Sample No.	CaO	MgO	P_2O_5	CaO	MgO	SiO_2	CaO	MgO	CO_2
1	70.81	19.30	9.89	65.80	17.93	16.27	51.84	14.13	34.03
2	76.41	11.23	12.36	75.22	11.06	13.72	62.34	9.16	28.50
3	74.27	14.16	11.57	71.77	13.68	14.55	57.03	10.87	32.09
4	75.62	10.73	13.65	76.88	10.91	12.21	63.54	9.02	27.44
5	71.80	17.59	10.61	68.40	16.76	14.84	54.59	13.37	32.04
6	73.73	17.64	8.63	66.00	15.97	18.21	52.69	12.61	34.70
7	75.36	15.52	9.12	69.32	14.28	16.40	55.73	11.48	32.79
8	74.44	14.78	10.77	71.24	14.15	41.61	56.81	11.28	31.90
9	76.64	11.73	11.63	75.47	11.55	12.98	61.70	9.40	29.20

TABLE-XX

Recalculated to 100 wt.% of the bulk components of (A) $CaO-MgO-P_2O_5$ (B) $CaO-MgO-SiO_2$ and (C) $CaO-MgO-CO_2$ in Gandhra phosphorites

	(A)			(B)			(C)		
Sample No.	CaO	MgO	P_2O_5	CaO	MgO	SiO_2	CaO	MgO	CO_2
10	69.02	17.70	13.28	67.34	17.27	15.38	56.13	14.39	29.48
11	75.43	7.90	16.67	79.58	8.33	12.08	71.65	7.50	20.85
12	81.90	7.29	10.81	81.84	7.28	10.87	60.05	5.34	34.61
13	77.89	12.56	9.55	74.55	12.02	13.43	54.15	8.73	37.12
14	83.01	6.48	10.51	85.05	6.64	8.15	59.66	4.65	35.68
15	75.47	14.79	9.73	67.96	13.32	18.72	51.37	10.07	38.57
16	78.07	9.52	12.41	76.89	9.38	13.73	63.61	7.76	28.63
17	71.92	11.41	16.67	76.21	12.09	11.70	63.11	10.01	26.88
18	82.52	4.47	13.02	89.88	4.87	5.25	73.47	3.98	22.85
19	73.85	11.72	14.42	81.96	13.01	5.02	69.63	11.05	19.32
20	67.80	15.63	16.57	77.39	17.83	4.78	55.78	12.85	31.37
21	74.33	14.71	10.97	77.67	15.37	6.96	59.55	11.78	28.66
22	75.91	12.72	11.37	75.82	12.71	11.47	59.35	9.95	30.70
23	75.90	11.27	12.83	78.22	11.62	10.16	62.78	9.32	27.90

TABLE-XXI

Recalculated to 100 wt.% of the bulk components of (A) $CaO-MgO-P_2O_5$ (B) $CaO-MgO-SiO_2$ and (C) $CaO-MgO-CO_2$ in Ambapani phosphorites

	(A)			(B)			(C)		
Sample No.	CaO	MgO	P_2O_5	CaO	MgO	SiO_2	CaO	MgO	CO_2
24	75.41	12.32	12.27	76.81	12.55	10.64	61.58	10.06	28.36
25	75.10	17.46	7.44	70.55	16.40	13.05	54.05	12.57	33.39
26	71.86	21.21	6.93	63.97	18.88	17.15	50.32	14.85	34.82
27	74.76	17.77	7.47	70.24	16.70	13.06	53.18	12.64	34.18
28	76.72	13.07	10.21	72.32	12.33	15.35	59.18	10.08	30.73
29	72.89	17.50	9.61	73.13	17.55	9.32	56.10	13.47	30.43
30	73.04	13.45	13.51	74.97	13.80	11.23	60.51	11.14	28.35
31	75.83	16.49	7.67	70.08	15.24	14.68	53.38	11.61	35.01
32	72.90	17.15	9.95	70.54	16.60	12.86	54.58	12.84	32.58

TABLE-XXII

Recalculated to 100 wt.% of the bulk components of (A) $CaO-MgO-P_2O_5$ (B) $CaO-MgO-SiO_2$ and (C) $CaO-MgO-CO_2$ in Ranjitpura phosphorites

Sample No.	(A)			(B)			(C)		
	CaO	MgO	P_2O_5	CaO	MgO	SiO_2	CaO	MgO	CO_2
33	67.32	15.64	17.04	69.65	16.18	14.17	58.62	13.62	27.76
34	66.85	14.28	18.87	70.74	15.11	14.11	59.29	12.67	28.04
35	69.07	14.58	16.35	69.07	14.58	16.35	57.66	12.17	30.17
36	66.64	12.88	20.49	74.00	14.30	11.70	59.55	11.51	28.94
37	64.89	14.22	20.89	75.14	16.47	8.39	59.51	13.04	27.45
38	67.24	11.45	21.31	77.49	13.20	9.31	61.70	10.51	27.80
39	67.49	14.06	18.52	71.40	14.88	13.71	58.79	12.26	28.95
40	67.17	10.71	22.12	78.55	12.52	8.92	63.00	10.04	26.96
41	65.11	13.95	20.94	72.92	15.62	11.46	58.50	12.53	28.96
42	61.75	13.99	24.26	75.62	17.14	7.24	63.60	14.41	21.99
43	63.35	12.48	24.17	76.31	15.04	8.65	62.14	12.25	25.61
44	67.27	18.26	14.47	65.83	17.87	16.30	54.87	14.89	30.24
45	64.82	11.71	23.47	75.50	13.64	10.86	62.54	11.30	26.16
46	63.79	15.67	20.53	69.01	16.95	14.04	56.73	13.94	29.93
47	64.65	10.34	25.01	77.24	12.36	10.40	62.58	10.01	27.41
48	63.38	9.56	27.05	79.84	12.05	8.13	67.93	10.25	21.81
49	64.90	12.36	22.74	75.44	14.37	10.19	60.61	11.55	27.84
50	62.50	10.98	26.52	78.78	13.85	7.34	65.84	11.57	22.58

TABLE-XXIII

Recalculated to 100 wt.% of the bulk components of (A) $MgO/CaO-SiO_2-H_2O^+$ (B) $MgO/CaO-SiO_2-CO_2$ and (C) $Na_2O-CaO-P_2O_5$ in Chalvad phosphorites

	(A)			(B)			(C)		
Sample No.	MgO/CaO	SiO_2	H_2O^+	MgO/CaO	SiO_2	CO_2	Na_2O	CaO	P_2O_5
1	2.46	90.97	6.56	0.73	27.16	72.11	0.78	87.06	12.16
2	1.52	89.53	8.94	0.48	28.38	71.13	0.74	85.44	13.82
3	1.99	93.19	4.82	0.56	26.34	73.10	1.19	85.49	13.32
4	1.58	88.18	10.24	0.48	26.75	72.77	1.17	83.72	15.11
5	2.40	91.30	6.30	0.70	26.80	72.50	-	87.12	12.88
6	2.01	94.56	3.43	0.62	29.34	70.04	0.95	88.67	10.38
7	1.94	97.45	4.61	0.59	28.51	70.90	0.79	88.50	10.71
8	2.06	93.91	4.03	0.58	26.60	72.81	0.74	86.71	12.55
9	1.65	91.63	6.72	0.48	26.44	73.08	0.23	86.62	13.15

TABLE-XXIV

Recalculated to 100 wt.% of the bulk components of (A) $MgO/CaO-SiO_2-H_2O^+$ (B) $MgO/CaO-SiO_2-CO_2$ and (C) $Na_2O-CaO-P_2O_5$ in Gandhra phosphorites

	(A)			(B)			(C)		
Sample No.	MgO/CaO	SiO_2	H_2O^+	MgO/CaO	SiO_2	CO_2	Na_2O	CaO	P_2O_5
10	2.43	90.65	6.92	0.80	30.07	69.13	1.52	82.59	15.89
11	1.13	91.41	7.46	0.42	34.13	65.44	1.30	80.83	17.87
12	1.26	89.75	8.99	0.26	18.68	81.05	1.00	87.45	11.55
13	1.93	93.02	5.05	0.43	20.72	78.85	0.45	88.68	10.87
14	1.52	88.95	9.52	0.24	13.78	85.98	2.07	86.92	11.01
15	1.74	90.59	7.67	0.51	26.70	72.79	0.93	87.64	11.32
16	1.31	91.90	6.78	0.40	28.28	71.31	0.46	85.89	13.65
17	2.01	89.18	8.81	0.59	26.35	73.06	0.77	80.56	18.67
18	1.20	81.73	17.07	0.23	15.95	83.81	0.46	85.98	13.56
19	3.60	75.90	20.50	0.85	17.93	81.21	0.77	83.02	16.21
20	6.30	73.97	19.73	0.84	9.81	89.36	1.47	79.18	19.35
21	3.74	80.34	15.92	0.73	15.57	83.70	1.89	85.49	12.62
22	2.10	87.04	10.86	0.54	22.51	76.95	1.49	85.68	12.83
23	2.04	84.26	13.70	0.54	22.50	76.99	1.45	84.30	14.25

TABLE-XXV

Recalculated to 100 wt.% of the bulk components of (A) $MgO/CaO-SiO_2-H_2O^+$ (B) $MgO/CaO-SiO_2-CO_2$ and (C) $Na_2O-CaO-P_2O_5$ in Ambapani phosphorites

	(A)			(B)			(C)		
Sample No.	MgO/CaO	SiO_2	H_2O^+	MgO/CaO	SiO_2	CO_2	Na_2O	CaO	P_2O_5
24	2.05	84.98	12.96	0.56	22.99	76.46	1.47	84.74	13.79
25	2.62	89.17	8.21	0.67	22.89	76.46	1.30	89.80	8.90
26	2.48	92.31	5.21	0.74	27.72	71.54	0.58	90.67	8.75
27	2.76	89.42	7.82	0.69	22.28	77.03	1.33	89.71	8.96
28	1.57	89.84	8.59	0.50	28.87	70.62	1.89	86.59	11.52
29	3.67	86.98	9.34	0.80	18.87	80.33	1.71	86.83	11.45
30	2.21	85.75	12.04	0.62	24.06	75.30	1.62	83.02	15.36
31	2.27	91.34	6.39	0.60	24.06	75.35	0.98	89.92	9.10
32	2.61	89.78	7.60	0.68	23.24	76.09	1.22	86.92	11.86

TABLE-XXVI

Recalculated to 100 wt.% of the bulk components of (A) $MgO/CaO-SiO_2-H_2O^+$ (B) $MgO/CaO-SiO_2-CO_2$ and (C) $Na_2O-CaO-P_2O_5$ in Ranjitpura phosphorites

	(A)			(B)			(C)		
Sample No.	MgO/CaO	SiO_2	H_2O^+	MgO/CaO	SiO_2	CO_2	Na_2O	CaO	P_2O_5
33	2.28	87.80	9.92	0.77	29.82	69.41	0.42	79.47	20.11
34	2.18	88.45	9.37	0.73	29.50	69.77	1.03	77.17	21.79
35	1.90	89.24	8.86	0.66	30.94	68.40	0.50	80.46	19.04
36	2.42	86.51	11.07	0.68	24.38	74.94	0.34	76.23	23.44
37	3.72	82.57	13.71	0.87	19.32	79.81	1.40	74.59	24.01
38	2.64	82.43	14.93	0.67	20.92	78.41	1.34	74.91	23.75
39	2.28	88.82	8.90	0.71	27.85	71.43	1.24	77.48	21.28
40	2.45	80.67	16.87	0.63	20.85	78.52	0.98	74.49	24.53
41	2.70	85.49	11.81	0.75	23.91	75.33	1.36	74.64	24.00
42	4.25	79.85	15.90	1.14	21.43	77.43	1.19	70.94	27.86
43	3.27	81.86	14.87	0.85	21.38	77.76	0.99	71.67	27.34
44	2.50	93.70	3.80	0.82	30.75	68.43	1.41	81.14	17.45
45	2.36	82.46	15.18	0.73	25.41	73.86	1.27	72.48	26.24
46	2.60	85.98	11.42	0.85	28.00	71.15	1.25	74.71	24.04
47	2.99	83.67	14.04	0.64	23.36	76.00	1.31	71.16	27.53
48	2.52	80.67	16.81	0.75	23.90	75.35	1.36	69.13	29.50
49	2.73	83.74	13.52	0.74	22.55	76.71	1.19	73.17	25.64
50	3.15	75.83	21.02	0.88	21.24	77.88	1.36	69.25	29.34

TABLE--XXVII

Recalculated to 100 wt.% of the bulk components of (A) P_2O_5-F-H_2O^+ and (B) SiO_2-Al_2O_3-K_2O in Chalvad phosphorites

Sample No.	(A)			(B)		
	P_2O_5	F	H_2O^+	SiO_2	Al_2O_3	K_2O
1	88.86	-	11.32	86.86	11.31	1.82
2	83.80	6.76	9.44	85.37	11.72	2.91
3	87.24	6.89	5.87	83.88	11.22	4.90
4	84.68	6.66	8.66	91.58	-	8.42
5	86.51	4.73	8.76	81.74	11.10	7.16
6	92.13	-	7.87	85.75	10.84	3.41
7	91.20	-	8.80	85.27	11.70	3.03
8	88.92	5.68	5.40	87.42	12.58	-
9	85.65	7.23	7.12	87.58	10.32	2.11

TABLE-XXVIII

Recalculated to 100 wt.% of the bulk components of (A) P_2O_5-F-H_2O^+ and (B) SiO_2 -Al_2O_3-K_2O in Gandhra phosphorites

	(A)			(B)		
Sample No.	P_2O_5	F	H_2O^+	SiO_2	Al_2O_3	K_2O
10	84.14	8.24	7.62	84.72	12.66	2.62
11	87.00	8.12	4.87	79.86	11.15	8.98
12	83.22	8.39	8.39	76.34	18.64	5.02
13	92.61	-	7.39	82.85	14.47	2.68
14	92.50	-	7.50	75.93	18.37	5.69
15	84.70	-	15.30	83.94	11.54	4.52
16	83.30	9.80	6.90	77.99	12.53	9.47
17	86.29	8.06	5.65	83.81	15.72	0.47
18	85.71	7.66	6.63	66.15	29.18	4.67
19	84.83	7.98	7.19	69.92	27.59	2.49
20	85.86	8.35	5.78	71.62	25.99	2.39
21	89.27	-	10.73	72.47	26.18	1.35
22	88.80	-	11.20	81.79	16.01	2.20
23	81.70	8.09	10.21	79.92	17.12	2.96

TABLE-XXIX

Recalculated to 100 wt.% of the bulk components of (A) P_2O_5-F-H_2O^+ and (B) SiO_2-Al_2O_3-K_2O in Ambapani phosphorites

Sample No.	(A)			(B)		
	P_2O_5	F	H_2O^+	SiO_2	Al_2O_3	K_2O
24	82.77	6.49	10.74	82.44	12.33	5.23
25	81.52	4.47	14.01	79.47	12.09	8.43
26	86.44	-	13.56	81.16	10.59	8.26
27	80.69	6.18	13.13	77.80	13.20	9.00
28	86.77	-	13.23	83.02	11.77	5.20
29	84.97	6.21	8.82	76.34	12.90	10.75
30	82.82	7.69	9.42	84.40	11.85	3.75
31	82.15	5.95	11.90	80.47	12.17	7.36
32	82.80	7.83	9.37	83.97	9.45	6.58

TABLE-XXX

Recalculated to 100 wt.% of the bulk components of (A) P_2O_5-F-H_2O^+ and (B) SiO_2-Al_2O_3-K_2O in Ranjitpura phosphorites

Sample No.	(A)			(B)		
	P_2O_5	F	H_2O^+	SiO_2	Al_2O_3	K_2O
33	91.67	-	8.33	82.79	13.38	3.83
34	87.53	5.91	6.56	80.72	13.39	5.89
35	85.60	5.90	8.50	77.36	14.90	7.74
36	88.13	6.07	5.80	83.29	13.33	7.74
37	89.39	5.46	5.15	77.71	15.29	7.00
38	88.76	5.14	6.10	73.20	18.23	8.56
39	88.37	5.44	6.19	78.65	13.56	7.79
40	88.71	4.89	6.40	78.04	13.95	8.01
41	88.74	5.27	5.99	78.82	16.09	5.09
42	90.46	5.15	4.39	77.84	16.40	5.77
43	90.35	4.77	4.88	78.77	14.46	6.76
44	95.54	-	4.46	83.00	12.32	4.68
45	88.95	4.54	6.51	80.25	14.14	5.61
46	88.27	4.31	7.41	81.58	12.81	5.62
47	89.83	4.92	5.25	78.49	15.05	6.45
48	90.87	4.61	4.52	100	-	-
49	89.03	5.42	4.54	77.09	16.16	6.75
50	89.93	4.58	5.49	86.25	13.75	-

TABLE-XXXI

Recalculated to 100 wt.% of the bulk components of (A) P_2O_5-H_2O^+-CO_2 and (B) P_2O_5-F-CO_2 in Chalvad phosphorites

Sample No.	(A)			(B)		
	P_2O_5	H_2O^+	CO_2	P_2O_5	F	CO_2
1	17.16	2.19	80.65	17.59	-	82.45
2	25.38	2.86	71.76	25.59	2.06	72.35
3	21.37	1.44	77.19	21.27	1.68	77.04
4	28.61	2.92	68.47	28.80	2.27	68.93
5	19.71	2.00	78.29	19.92	0.96	79.12
6	14.90	1.27	83.82	15.09	-	84.91
7	16.78	1.62	81.60	17.10	-	82.94
8	20.24	1.23	78.53	19.72	1.30	78.98
9	23.72	1.97	74.31	23.71	2.00	74.29

TABLE-XXXII

Recalculated to 100 wt.% of the bulk components of (A) P_2O_5-H_2O^+-CO_2 and (B) P_2O_5-F-CO_2 in Gandhra phosphorites

Sample No.	(A)			(B)		
	P_2O_5	H_2O^+	CO_2	P_2O_5	F	CO_2
10	26.18	2.37	71.45	26.13	2.56	71.31
11	42.15	2.36	55.49	41.49	3.87	54.63
12	18.29	1.84	79.86	18.29	1.84	79.86
13	14.99	1.20	83.81	15.26	-	84.83
14	17.23	1.40	81.37	17.48	-	82.52
15	14.28	2.58	83.14	14.66	-	85.34
16	25.55	2.12	72.34	25.32	2.98	71.70
17	34.45	2.25	63.30	34.12	3.19	62.69
18	33.08	2.56	64.36	32.95	2.94	70.57
19	39.91	3.38	56.71	39.76	3.74	56.50
20	29.69	2.00	68.31	29.42	2.86	67.71
21	22.82	2.74	74.44	23.46	-	76.54
22	21.84	2.75	75.41	22.46	-	77.54
23	26.64	3.33	70.03	26.83	2.66	70.52

TABLE-XXXIII
Recalculated to 100 wt.% of the bulk components of (A) P_2O_5-H_2O^+-CO_2 and (B) P_2O_5-F-CO_2 in Ambapani phosphorites

Sample No.	(A)			(B)		
	P_2O_5	H_2O^+	CO_2	P_2O_5	F	CO_2
24	25.25	3.28	71.47	25.58	2.00	72.41
25	13.50	2.32	84.18	13.72	0.75	85.53
26	12.01	1.88	86.11	12.24	-	87.76
27	13.16	2.14	84.70	13.31	1.02	85.66
28	19.79	3.02	77.20	20.40	-	79.60
29	19.17	1.99	78.84	19.29	1.41	79.30
30	27.43	3.12	69.45	27.58	2.56	69.86
31	13.11	1.90	84.99	13.23	0.96	85.81
32	18.22	2.06	79.72	18.28	1.73	79.99

TABLE-XXXIV

Recalculated to 100 wt.% of the bulk components of (A) P_2O_5-H_2O^+-CO_2 and (B) P_2O_5-F-CO_2 in Ranjitpura phosphorites

Sample No.	(A)			(B)		
	P_2O_5	H_2O^+	CO_2	P_2O_5	F	CO_2
33	33.76	3.07	63.17	34.83	-	65.22
34	36.36	2.73	60.91	36.46	2.46	61.08
35	30.21	3.00	66.79	30.49	2.10	67.41
36	37.78	2.49	59.73	37.74	2.60	59.67
37	40.15	2.31	57.54	40.10	2.45	57.45
38	40.16	2.76	57.08	40.33	2.34	57.33
39	31.92	2.45	62.63	35.03	2.16	62.81
40	42.17	3.04	54.78	42.48	2.34	55.18
41	38.36	2.59	59.05	38.48	2.29	59.23
42	51.84	2.51	45.64	51.62	2.94	45.44
43	46.85	2.53	50.62	46.87	2.47	50.65
44	27.71	1.29	71.00	28.07	-	71.93
45	44.87	3.28	51.84	45.32	2.32	52.36
46	37.17	3.12	59.71	37.66	1.85	60.49
47	45.65	2.61	51.69	45.72	2.51	51.77
48	55.49	2.76	41.75	55.46	2.81	41.73
49	42.13	2.62	55.25	42.16	2.57	55.28
50	53.50	3.27	43.23	53.79	2.74	43.47

TABLE-XXXV: Correlation coefficient of nine Chalvad phosphorite samples.

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	CaO	MgO	P_2O_5	FeO	Na_2O	K_2O	H_2O^+	CO_2	F	Cu	Ni	Co	Pb	Zn	Cr	Sr	Rb	Li	Cd
SiO_2	1 00																							
Al_2O_3	0 71	1 00																						
TiO_2	0 56	0 24	1 00																					
Fe_2O_3	0 79	0 56	0 29	1 00																				
MnO	0 90	0 77	0 61	0 82	1 00																			
CaO	-0 82	-0 70	-0 44	-0 54	-0 78	1 00																		
MgO	0 69	0 58	0 45	0 27	0 74	-0 95	1 00																	
P_2O_5	-0 93	-0 82	-0 83	-0 68	-0 71	-0 91	-0 79	1 00																
FeO	0 41	-0 24	-	-0 51	-0 59	0 44	-0 31	0 39	1 00															
Na_2O	-	-0 43	-	0 29	-	0 23	-0 38	0 31	-0 28	1 00														
K_2O	-	0 43	-	-	-	-	-	0 21	-0 56	-	1 00													
H_2O^+	-0 55	-0 64	-	-0 50	-0 42	0 57	-0 39	0 70	0 54	-	0 30	1 00												
CO_2	0 88	0 75	-	0 68	0 76	-0 95	0 87	-0 95	-0 33	-	-	-0 70	1 00											
F	-0 91	0 63	-0 64	-0 64	-0 80	0 89	-0 81	0 93	-	-	-	0 46	-0 89	1 00										
Cu	-0 79	-0 66	-	-0 74	-0 48	0 51	-0 32	-0 31	0 23	-0 44	-	0 40	-0 60	0 61	1 00									
Ni	0 81	0 58	-	0 94	0 77	-0 48	0 24	-0 66	-0 32	0 21	-	-0 49	0 59	-0 59	-0 70	1 00								
Co	0 68	0 47	0 37	0 77	0 73	-0 28	-	-0 44	-0 62	0 22	-	-0 32	0 36	-0 35	-0 29	0 85	1 00							
Pb	-0 65	-0 66	-0 28	-0 53	-0 37	0 46	-0 30	0 76	-	-	0 48	0 78	-0 60	0 64	0 36	-0 52	-0 34	1 00						
Zn	-0 48	-0 47	-	-	-0 45	0 80	-0 89	0 60	-	0 29	-	-	-0 73	0 66	0 42	-	-	-	1 00					
Cr	0 75	0 42	-	0 78	0 62	-0 37	-	-0 55	-0 42	0 28	-	-0 52	0 54	-0 46	-0 58	0 91	0 87	-0 49	-	1 00				
Sr	-0 77	-0 78	-0 46	-0 55	-0 81	0 90	-0 81	0 86	0 55	0 26	-	-0 68	-0 85	0 74	0 27	-0 47	-0 44	0 53	0 54	-0 39	1 00			
Rb	-	-0 39	-	-	-	-	-	-	-0 61	-	0 97	0 31	-	-	-	-	-	0 52	-	-0 21	-	1 00		
Li	0 43	-	-	0 77	0 63	-	-	-0 25	-0 29	0 40	-	-	-	-0 24	-0 71	0 83	0 62	-0 25	-	0 73	-	-	1 00	
Cd	0 29	0 67	-	-	-0 27	0 36	-0 34	0 50	-0 32	0 47	0 71	0 60	-0 44	0 34	-	-	-	0 68	-	-	0 50	0 62	-	1 00

** Values less than or equal to 0 20 are omitted*

TABLE-XXXVI: Correlation coefficient of fourteen Gandhra phosphorite samples.

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	CaO	MgO	P_2O_5	FeO	Na_2O	K_2O	H_2O^+	CO_2	F	Cu	Ni	Co	Pb	Zn	Cr	Sr	Rb	Li	Cd
SiO_2	1.00																							
Al_2O_3	0.80	1.00																						
TiO_2	-	-	1.00																					
Fe_2O_3	0.58	-	0.42	1.00																				
MnO	-	-	-	-0.26	1.00																			
CaO	-0.59	-	-	-0.43	-	1.00																		
MgO	-	-	-	-0.25	0.74	-0.47	1.00																	
P_2O_5	-0.37	-0.45	-0.53	-0.59	-	0.53	-	1.00																
FeO	-	-	-	-0.22	0.38	-0.29	0.38	-	1.00															
Na_2O	-0.27	-0.32	0.42	-	-	-	0.21	-	-	1.00														
K_2O	0.54	-	-	0.67	-0.34	-	-0.40	-	-0.41	-	1.00													
H_2O^+	-	0.23	-	-	0.28	-	0.53	-	0.27	-	-0.27	1.00												
CO_2	0.22	-	0.38	0.44	-	-0.69	-	-0.71	-	-	-	-0.38	1.00											
F	-	-029	-0.64	-0.32	-	0.42	-	0.85	-	-	-	-	-0.74	1.00										
Cu	0.37	0.29	-	-	-	-0.30	0.27	-0.29	-0.41	-	-	-	-	-	1.00									
Ni	-	-	0.38	-	-	-	-0.27	-	-	0.43	-0.27	-	-	-0.36	-	1.00								
Co	0.48	0.51	0.44	0.41	0.48	-	-	-0.47	-	-	0.24	0.36	-	-0.48	0.37	-	1.00							
Pb	0.25	-	0.27	-	-	-	-	-	-0.55	0.67	-	-	-	-0.25	0.53	0.45	0.49	1.00						
Zn	-	-0.61	-	-0.31	-	-	-	-	0.28	0.23	-0.29	-	-	-	-	0.71	-	0.25	1.00					
Cr	0.68	-	-0.24	0.31	-	-0.49	-	-	-	-	0.32	-	-	-	0.22	-	0.23	-	0.38	1.00				
Sr	0.48	-	-0.47	-	-0.44	-	-	0.45	-	-	0.38	-	-0.39	0.50	-	-	-	-	0.49	0.57	1.00			
Rb	0.58	-	-	0.76	-0.21	-	-0.34	-0.23	-0.25	-0.30	0.89	-	-	-	-	-	0.42	-	-	0.45	0.30	1.00		
Li	-	0.27	0.24	-	0.76	-	-0.49	-	0.25	0.34	-	0.44	-	-0.22	-	-0.26	0.65	0.35	-	-	-	-	1.00	
Cd	-	-	-0.21	-	-0.60	0.42	-0.47	-	-0.35	-0.35	0.23	0.37	-0.24	0.36	-0.27	-	-0.48	-0.28	-	-0.42	0.25	-	-0.72	1.00

* *Values less than or equal to 0.20 are omitted.*

TABLE-XXXVII: Correlation coefficient of nine Ambapani phosphorite samples.

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	CaO	MgO	P_2O_5	FeO	Na_2O	K_2O	H_2O^+	CO_2	F	Cu	Ni	Co	Pb	Zn	Cr	Sr	Rb	Li	Cd
SiO_2	1 00																							
Al_2O_3	0 34	1 00																						
TiO_2	0 47	0 34	1 00																					
Fe_2O_3	-	0 39	0 30	1 00																				
MnO	-	-	-	0 78	1 00																			
CaO	-0 54	-0 56	-0 35	-0 66	-0 64	1 00																		
MgO	0 22	-	0 31	0 38	0 60	-0 80	1 00																	
P_2O_5	-0 53	-0 67	-0 49	-0 81	-0 71	0 93	-0 63	1 00																
FeO	-0 86	-0 64	0 52	-	-	0 51	-0 78	0 56	1 00															
Na_2O	-0 56	-0 44	-0 29	-0 36	0 51	0 86	-0 70	0 74	0 50	1 00														
K_2O	0 50	0 63	0 55	0 67	0 70	-0 91	-0 79	-0 94	-0 54	-0 74	1 00													
H_2O^+	-0 21	-0 24	-0 48	-0 57	-0 71	0 79	-0 84	0 81	0 43	0 69	-0 58	1 00												
CO_2	0 58	0 60	0 44	0 64	0 60	-0 86	0 68	-0 95	-0 63	-0 87	0 88	-0 86	1 00											
F	-0 77	-0 85	-0 66	-0 55	-0 24	0 58	-0 31	0 74	0 75	0 38	-0 74	0 39	-0 60	1 00										
Cu	-	0 34	-0 39	-0 28	-0 39	0 27	-0 38	-	-	0 22	-	0 39	-	-	1 00									
Ni	0 65	0 77	0 38	0 60	0 69	-0 82	0 58	-0 89	-0 57	-0 78	0 91	-0 61	0 83	-0 79	-	1 00								
Co	0 56	0 54	0 30	0 61	0 64	-0 94	0 69	-0 88	-0 47	-0 95	0 83	-0 74	0 93	-0 51	-0 23	0 81	1 00							
Pb	-	-	-	-	-0 55	0 47	-0 50	0 41	-	0 75	-0 43	0 48	-0 52	-	0 27	-0 51	-0 67	1 00						
Zn	-0 56	-0 49	-	-	-0 29	0 83	-0 67	0 64	0 51	0 86	-0 67	0 70	-0 82	0 31	-	-0 62	-0 81	0 45	1 00					
Cr	0 65	0 78	0 25	0 61	0 57	-0 90	0 58	-0 86	-0 48	-0 84	0 30	-0 62	0 92	-0 68	-	0 93	0 90	-0 45	-0 77	1 00				
Sr	-0 31	-0 37	-0 39	-0 65	-0 66	0 92	-0 84	0 86	0 43	0 66	-0 88	0 96	-0 88	0 48	0 33	-0 66	-0 75	0 34	0 72	-0 70	1 00			
Rb	0 39	0 62	-	0 68	0 75	-0 86	0 67	-0 89	-0 30	-0 72	0 92	-0 71	0 82	-0 60	-	0 92	0 83	-0 52	-0 63	0 91	-0 77	1 00		
Li	-0 51	-0 48	-0 68	-0 58	-0 59	0 79	-0 59	0 80	0 55	0 53	-0 75	0 72	-0 79	0 57	0 34	-0 67	0 83	0 36	0 65	-0 74	0 67	-0 58	1 00	
Cd	0 24	-	-0 34	-0 47	-0 75	0 38	-0 41	0 53	-	-	-0 60	0 65	-0 40	-0 27	-	-0 39	-0 27	-	-	-0 32	0 56	-0 55	0 40	1 00

** Values less than or equal to 0 20 are omitted*

TABLE-XXXVIII: Correlation coefficient of eighteen Ranjitpura phosphorite samples.

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	CaO	MgO	P_2O_5	FeO	Na_2O	K_2O	H_2O^+	CO_2	F	Cu	Ni	Co	Pb	Zn	Cr	Sr	Rb	Li	Cd
SiO_2	1.00																							
Al_2O_3	0.74	1.00																						
TiO_2	0.68	0.53	1.00																					
Fe_2O_3	0.84	0.46	0.63	1.00																				
MnO	0.85	0.66	0.62	0.66	1.00																			
CaO	-0.75	-0.43	-0.52	-0.66	-0.63	1.00																		
MgO	0.51	0.45	0.22	0.39	-	-0.36	1.00																	
P_2O_5	-0.84	-0.87	-0.60	-0.69	-0.76	0.47	-0.57	1.00																
FeO	-0.59	-0.39	-0.30	-0.60	-0.60	0.62	-0.38	0.48	1.00															
Na_2O	-0.57	-0.56	-0.46	-0.45	-0.40	0.28	*-0.24*	*0.62*	*0.40*	*1.00*														
K_2O	0.47	0.75	0.24	0.30	0.49	-	-	-0.63	-	-0.39	1.00													
H_2O^+	-0.31	-0.26	-0.23	-	-0.29	0.23	-0.57	0.53	-	-	-0.38	1.00												
CO_2	0.77	0.89	0.51	0.53	0.75	-0.43	0.38	-0.35	-0.44	-0.53	0.75	-0.43	1.00											
F	-0.75	-0.54	-0.44	-0.44	-0.73	0.41	-0.64	0.74	0.51	0.41	-0.27	0.46	-0.60	1.00										
Cu	0.85	0.49	0.64	0.80	0.71	-0.59	0.42	-0.72	-0.60	-0.52	-	-0.34	0.52	-0.68	1.00									
Ni	0.39	-	0.34	0.31	0.27	-0.57	-	-	-	-	-0.26	-0.24	-	-	0.43	1.00								
Co	-	-0.24	-	-	-	-	-	-	-	-	-	-	-	-	-	0.35	1.00							
Pb	0.34	0.28	0.27	0.39	0.36	-	-	0.37	-0.35	-0.38	-	-	0.21	-0.45	0.54	-0.24	-	1.00						
Zn	-0.40	-0.35	-0.24	-0.35	-0.24	-	-	0.45	0.26	0.48	-0.22	-	-0.50	-	-0.50	-	-	-0.28	1.00					
Cr	-	-	-	-0.21	-	0.30	-	-	-	-	-	-	-	-0.21	-	-	-	-	-	1.00				
Sr	-0.72	-0.80	-0.52	-0.52	-0.57	0.26	-0.52	0.92	0.25	0.67	-0.69	0.50	-0.88	0.61	-0.55	-	-	-0.32	0.49	-	1.00			
Rb	0.24	0.37	-	-	0.33	-	-	-	-0.38	-	0.55	-	0.48	-	-	-	-	0.29	-0.31	-0.39	-0.29	1.00		
Li	-	-	-	-	-	-	-0.39	-	-	-0.29	-	0.39	-	-	-	-	-	-	-0.42	-	-	-	1.00	
Cd	-0.56	-0.46	-0.42	-0.53	-0.27	0.23	-0.37	0.55	0.30	0.50	-0.37	-	-0.41	0.34	-0.41	-	-	-	0.37	0.35	0.46	-0.37	-	1.00

** Values less than or equal to 0.20 are omitted.*

TABLE-XXXIX

Trace elements analyses of Chalvad phosphorite samples

Elements (ppm)	1	2	3	4	5	6	7	8	9	Mean (x)	Standard Deviation (S.D.)
Cu	-	6	-	4	7	-	-	5	4	2.89	2.89
Ni	46	51	60	23	29	88	64	33	38	48	20.38
Co	43	72	59	42	48	91	60	51	40	56.22	16.64
Pb	51	58	54	69	51	28	18	30	39	44.22	16.47
Zn	33	78	62	81	56	64	67	70	72	64.78	14.22
Cr	87	93	100	78	72	143	96	90	87	94	20.30
Sr	112	200	116	281	49	46	92	88	262	138.44	87.91
Rb	5	7	13	19	23	10	7	-	-	9.33	7.89
Li	2	3	4	2	-	5	4	-	3	2.56	1.74
Cd	5	6	7	10	5	6	4	-	5	4.22	2.65

TABLE-XL

Trace elements analyses of Gandhra phosphorite Samples

Elements (ppm)	10	11	12	13	14	15	16	17	18	19	20	21	22	23	Mean (x)	Standard Deviation (S.D.)
Cu	6	-	3	3	-	-	-	-	-	-	-	-	4	5	1.50	2.21
Ni	41	48	39	49	72	28	33	64	45	30	31	48	69	52	46.36	14.22
Co	64	54	47	55	46	63	64	41	51	48	33	72	70	61	54.93	11.32
Pb	60	60	36	33	52	17	22	15	14	15	13	54	46	55	35.14	18.89
Zn	45	50	40	48	55	31	44	89	33	41	37	53	58	70	50.29	15.39
Cr	109	129	125	90	41	117	122	155	47	12	83	94	122	94	95.71	39.29
Sr	209	359	216	131	139	176	196	350	100	178	91	89	140	191	183.07	83.90
Rb	2	13	6	5	2	12	17	-	3	-	-	-	8	7	5.36	5.48
Li	2	2	1	1	-	2	2	-	1	1	2	5	2	2	1.64	1.21
Cd	7	8	8	8	9	7	8	8	8	10	6	5	5	7	7.43	1.40

TABLE-XLI

Trace elements analyses of Ambapani phosphorite samples

Elements (ppm)	24	25	26	27	28	29	30	31	32	Mean (x)	Standard Deviation (S.D.)
Cu	4	-	-	6	5	-	5	7	-	0.30	2.96
Ni	43	61	86	70	49	43	20	60	41	52.56	19.16
Co	40	63	71	60	39	42	38	62	54	52.11	12.54
Pb	15	27	13	20	50	31	42	21	16	26.11	12.79
Zn	88	69	32	52	81	72	64	39	60	61.89	18.44
Cr	29	98	134	110	48	34	25	98	42	68.67	41.12
Sr	265	101	58	64	179	81	210	89	98	127.22	72.84
Rb	7	20	28	30	7	14	-	17	8	14.56	10.15
Li	5	-	-	4	4	3	5	-	3	2.67	2.12
Cd	7	5	6	4	8	-	10	3	9	5.78	3.15

TABLE-XLII

Trace elements analyses of Ranjitpura phosphorite samples

Elements (ppm)	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	Mean (X)	Standard Devaition (S.D.)
Cu	7	6	8	3	-	3	4	-	3	-	-	7	-	3	-	3	-	2	2.72	2.68
Ni	27	29	91	38	25	31	52	37	39	29	51	86	39	53	44	80	52	54	47.28	19.43
Co	61	63	28	53	49	38	51	52	71	40	49	30	69	39	37	70	49	31	48.89	13.47
Pb	41	40	14	17	9	31	18	17	13	5	17	20	9	-	11	13	-	16	16.17	11.12
Zn	59	67	33	41	60	64	59	70	32	94	79	81	86	63	72	71	110	82	67.94	19.43
Cr	90	40	27	65	113	60	-	62	61	-	40	71	110	51	60	53	61	82	55.89	30.98
Sr	138	169	101	140	158	181	189	216	185	275	207	111	223	190	302	351	230	381	208.17	74.84
Rb	3	8	7	9	-	18	30	19	21	-	20	17	8	11	7	-	-	6	10.22	8.52
Li	3	2	7	4	3	3	-	6	5	-	6	-	4	-	5	-	-	5	2.94	2.39
Cd	6	7	5	8	8	9	6	6	8	6	10	8	8	6	8	9	9	10	7.61	1.46

TABLE-XLIII

Trace elements analyses of dolomitic limestone, quartzites and phyllites of Chalvad, Gandhra, Ambapani and Ranjitpura blocks, Panchmahals.

Elements	Dolomitic limestone				Quartzites				Phyllites		
(ppm)	DL-1	DL-2	DL-3	Mean (x)	Q-1	Q-2	Q-3	Mean (x)	P-1	P-2	Mean (x)
Cu	30	32	27	2.97	98	104	82	94.67	16	27	21.5
Ni	40	36	37	37.67	51	59	28	46	49	34	41.5
Co	50	43	44	45.67	34	39	-	24.33	29	27	28
Pb	11	13	17	13.67	10	8	-	6	17	10	13.5
Zn	28	26	33	29.00	21	24	16	20.33	49	31	40
Cr	27	16	21	21.33	100	97	132	109.67	131	120	125.5
Sr	41	32	58	43.67	65	76	67	69.33	84	76	80
Rb	6	-	9	5	13	9	17	13	78	81	79.5
Li	4	-	5	3	-	8	-	2.67	17	11	14
Cd	5	5	6	5.33	7	-	7	4.67	-	8	4

TABLE-XLIV

Ni/Al x 10^{-3}, Ni/Mg x 10^{-4}, Ni/Fe x 10^{-3}, Co/Ni, Zn/Pb, Zn/Fe x 10^{-3}, Zn/Ca x10^{-4}, Cr/Al x 10^{-2}, Sr/Ca x 10^{-4}, Rb/Sr, Rb/Al x 10^{-4}, K/Rb x 10^{4} and Li/Mg x 10^{-5} ratios for Chalvad phosphorites

S.No.	Ni/Al x 10^{-3}	Ni/Mg x 10^{-4}	Ni/Fe x 10^{-3}	Co/Ni	Zn/Pb	Zn/Fe x 10^{-3}	Zn/Ca x 10^{-4}	Cr/Al x 10^{-2}	Sr/Ca x 10^{-4}	Rb/Sr	Rb/Al x 10^{-4}	K/Rb x 10^{4}	Li/Mg x 10^{-5}
1	6.67	6.94	3.83	0.93	0.65	2.75	1.14	1.26	3.88	0.05	7.2	3.4	3.0
2	7.97	11.91	4.04	1.14	1.34	6.20	2.26	1.45	5.79	0.04	10.9	3.6	7.0
3	9.52	11.88	3.55	0.98	1.15	3.67	1.98	1.59	3.70	0.11	20.6	3.3	7.9
4	-	5.45	3.38	1.83	1.17	1.19	0.44	-	7.97	0.07	-	3.1	4.7
5	4.39	4.66	0.00	1.65	1.10	6.67	1.86	1.09	1.63	0.47	34.8	2.9	-
6	11.58	14.86	4.17	1.03	2.29	3.03	2.18	1.88	1.57	0.22	13.2	3.7	8.4
7	9.28	12.03	3.18	0.94	3.72	3.33	2.18	1.39	3.01	0.08	9.5	4.1	7.5
8	4.78	6.21	3.71	1.54	2.33	7.86	0.45	1.30	2.78	-	-	-	-
9	7.31	8.52	5.28	1.05	1.85	10.0	2.08	1.73	7.58	-	-	3.4	6.7

TABLE-XLV

Ni/Al x 10^{-3}, Ni/Mg x 10^{-4}, Ni/Fe x 10^{-3}, Co/Ni, Zn/Pb, Zn/Fe x 10^{-3}, Zn/Ca x10^{-4}, Cr/Al x 10^{-2}, Sr/Ca x 10^{-4}, Rb/Sr, Rb/Al x 10^{-4}, K/Rb x 10^{4} and Li/Mg x 10^{-5} ratios for Gandhra phosphorites

S.No.	Ni/Al x 10^{-3}	Ni/Mg x 10^{-4}	Ni/Fe x 10^{-3}	Co/Ni	Zn/Pb	Zn/Fe x 10^{-3}	Zn/Ca x 10^{-4}	Cr/Al x 10^{-2}	Sr/Ca x 10^{-4}	Rb/Sr	Rb/Al x 10^{-4}	K/Rb x 10^{4}	Li/Mg x 10^{-5}
10	5.32	6.24	3.56	1.56	0.75	3.91	1.48	1.42	6.82	0.01	2.60	12.5	3.04
11	8.00	14.24	4.85	1.13	0.83	5.05	1.31	2.15	9.43	0.04	21.67	5.8	5.93
12	4.70	15.11	2.79	1.21	1.11	2.86	1.16	1.50	6.23	0.03	7.23	5.8	3.87
13	6.90	11.75	7.10	1.12	1.45	6.96	1.57	1.27	4.27	0.04	7.04	4.2	2.40
14	12.0	31.72	5.0	0.64	1.06	3.82	1.58	0.68	3.99	0.01	3.33	14.5	-
15	3.68	6.26	1.34	2.25	1.82	1.48	1.15	1.54	0.15	0.07	15.79	3.8	4.48
16	4.65	9.54	1.60	1.94	2.00	2.14	1.30	1.72	0.17	0.09	23.94	5.0	5.78
17	9.14	14.51	14.54	0.64	5.93	20.23	2.69	2.21	10.6	-	-	-	-
18	5.70	23.68	6.08	1.13	2.36	4.46	-	0.60	1.09	0.03	3.80	1.0	5.26
19	4.29	5.69	7.50	1.60	2.73	10.25	1.04	0.17	0.22	-	-	-	1.90
20	5.96	5.10	4.08	1.06	2.85	4.87	0.84	1.60	2.91	-	-	-	3.29
21	5.85	8.39	6.76	1.50	0.98	7.46	1.55	1.15	0.38	-	-	-	8.74
22	9.45	14.65	4.96	1.01	1.26	4.17	1.74	1.67	0.24	0.06	10.96	2.0	4.25
23	7.43	12.15	4.60	1.17	1.27	6.19	2.04	1.34	0.18	0.04	10.00	2.7	4.67

TABLE-XLVI

Ni/Al x 10^{-3}, Ni/Mg x 10^{-4}, Ni/Fe x 10^{-3}, Co/Ni, Zn/Pb, Zn/Fe x 10^{-3}, Zn/Ca x10^{-4}, Cr/Al x 10^{-2}, Sr/Ca x 10^{-4}, Rb/Sr, Rb/Al x 10^{-4}, K/Rb x 10^{4} and Li/Mg x 10^{-5} ratios for Ambapani phosphorites

S.No.	Ni/Al x 10^{-3}	Ni/Mg x 10^{-4}	Ni/Fe x 10^{-3}	Co/Ni	Zn/Pb	Zn/Fe x 10^{-3}	Zn/Ca x 10^{-4}	Cr/Al x 10^{-2}	Sr/Ca x 10^{-4}	Rb/Sr	Rb/Al x 10^{-4}	K/Rb x 10^{4}	Li/Mg x 10^{-5}
24	8.27	9.13	5.06	0.93	5.87	10.48	2.58	0.56	7.75	0.03	1.35	5.0	10.6
25	9.68	10.29	2.56	1.03	2.56	0	2.28	1.56	3.34	0.20	3.17	3.5	-
26	11.47	11.97	6.47	0.83	2.46	2.41	1.11	1.79	2.01	0.48	3.73	3.3	-
27	10.0	11.76	3.74	0.86	2.60	2.78	1.73	1.57	2.14	0.47	4.29	2.5	6.60
28	6.71	10.40	3.66	0.80	1.62	6.04	2.47	0.66	5.46	0.04	0.96	7.3	8.50
29	8.43	6.67	3.09	0.98	2.32	5.18	2.26	0.67	2.54	0.17	2.75	4.7	4.7
30	3.85	3.87	3.64	1.90	1.52	4.64	1.92	0.48	6.30	-	-	-	10.3
31	8.45	10.81	4.26	1.03	1.86	2.77	1.29	1.38	2.94	0.19	2.39	3.9	-
32	8.72	6.66	3.04	1.32	3.75	4.48	1.93	0.89	3.16	0.08	1.70	6.4	4.9

TABLE-XLVII

Ni/Al x 10^{-3}, Ni/Mg x 10^{-4}, Ni/Fe x 10^{-3}, Co/Ni, Zn/Pb, Zn/Fe x 10^{-3}, Zn/Ca x10^{-4}, Cr/Al x 10^{-2}, Sr/Ca x 10^{-4}, Rb/Sr, Rb/Al x 10^{-4}, K/Rb x 10^{4} and Li/Mg x 10^{-5} ratios for Ranjitpura phosphorites

S.No.	Ni/Al x 10^{-3}	Ni/Mg x 10^{-4}	Ni/Fe	Co/Ni	Zn/Pb	Zn/Fe x 10^{-3}	Zn/Ca x 10^{-4}	Cr/Al x 10^{-2}	Sr/Ca x 10^{-4}	Rb/Sr	Rb/Al x 10^{-4}	K/Rb x 10^{4}	Li/Mg x 10^{-5}
33	3.55	4.43	2.18	2.26	1.44	4.76	1.90	1.18	4.44	0.02	3.95	11.3	4.92
34	3.83	5.29	1.38	2.17	1.67	3.19	2.21	0.53	5..56	0.05	10.67	6.5	3.65
35	10.83	17.14	4.87	0.31	2.36	1.76	1.11	0.32	3.39	0.07	8.33	4.7	13.21
36	5.51	7.58	4.28	1.39	2.41	4.61	1.33	0.94	4.56	0.06	13.04	6.2	7.98
37	4.90	4.32	3.68	1.96	6.67	8.82	1.78	2.22	4.69	-	-	-	5.19
38	4.43	6.84	4.19	1.23	2.06	8.65	1.93	0.86	5.47	0.10	25.71	2.8	6.62
39	6.93	9.70	3.94	0.98	3.28	4.47	1.94	-	6.21	0.16	40.0	2.2	-
40	7.40	8.31	4.40	1.40	4.12	8.33	2.12	1.24	6.53	0.09	38.0	2.4	13.48
41	5.42	7.12	4.06	1.82	2.46	3.33	1.06	0.29	6.11	0.11	29.17	1.7	9.12
42	5.41	4.70	4.75	1.38	18.8	15.41	2.91	-	8.52	-	-	-	-
43	10.41	10.34	7.85	0.96	4.65	12.1	2.50	0.82	6.55	0.10	40.82	1.8	12.17
44	10.89	12.87	6.14	0.35	4.05	5.79	2.78	0.90	3.80	0.15	21.52	2.8	-
45	6.72	8.18	4.19	1.77	9.89	9.25	2.75	1.90	7.13	0.04	13.79	4.6	8.39
46	7.68	8.79	3.68	0.74	-	4.37	2.17	0.74	6.53	0.06	15.94	4.3	-
47	7.46	10.50	7.33	0.84	6.55	12.0	2.32	1.02	9.74	0.02	11.86	5.7	11.93
48	-	18.65	1.03	0.87	5.46	9.1	2.27	-	11.24	-	-	-	-
49	8.0	10.5	5.98	0.94	-	12.64	3.57	0.94	7.47	-	-	-	-
50	14.5	11.0	6.07	0.57	5.12	9.21	2.60	2.22	12.09	0.02	16.22	-	10.18

TABLE-XLVIII

Comparison of the abundance of trace elements of phosphorites

Elements (ppm)	I	II	III	IV	V	VI	VII	VIII
Cu	2.89	2.21	2.96	2.72	4-40	100	0.6-394	39
Ni	20.38	14.22	19.16	47.28	4-200	100	1.9-30	43
Co	16.64	11.32	12.54	48.89	-	<10	0.6-11.8	-
Pb	16.47	18.89	12.79	16.17	-	<10	0-100	-
Zn	14.22	15.39	18.44	67.94	10-200	300	4-345	213
Cr	20.30	39.29	41.12	55.89	30-400	1000	7-1600	220
Sr	87.91	83.90	72.84	208.17	50-1000	1000	1800-2000	974
Rb	7.89	5.48	10.15	10.22	-	-	0-100	-
Li	1.74	1.21	2.12	2.94	-	-	1-10	-
Cd	2.65	1.40	3.15	7.61	-	<50	1-10	-

I *Average of nine phosphorite samples from Chalvad.*
II *Average of fourteen phosphorite samples from Gandhra.*
III *Average of nine phosphorite samples from Ambapani.*
IV *Average of eighteen phosphorite samples from Ranjitpura.*
V *Average computed by Krauskopf (1955).*
VI *Threshold values for Phosphoria Formation according to Gulbrandsen (1966).*
VII *Average computed by Tooms et al., (1969) using data computed by Swaine (1962).*
VIII *Average computed for Moroccan phosphorites by Prevot and Lucas (1979).*